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Habilitation thesis

Bubble-particle interactions during the flotation of plastics

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I hereby declare that I have worked out this thesis independently and listed all the resources employed as well as co-authors of the presented results.

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Abstract

The sharp increase of plastic wastes has resulted in great social and environmental pressures and recycling, as an effective way currently available to reduce the negative impacts of plastic wastes, represents one of the most dynamic areas in the plastics industry today. Flotation is a promising method to solve the key problem of the recycling process, namely separation of plastic mixtures. Flotation enables the separation of hydrophobic materials from hydrophilic and it is based on the ability of some solids to remain attached to the bubble surface.

The present habilitation thesis summarises, in the form of comments, the results of my work focused on bubble behaviour and bubble-particle interactions in flotation, concentrating on the flotation of plastics. The thesis is divided into three major chapters. The first describes the basic principles of plastics flotation including processes and chemicals used during the flotation process. The second chapter is the basic principles and also differences between mineral and plastic flotation are compared in the beginning. Then the fundamental processes, collision of a spherical bubble with a falling spherical particle and attachment of the bubble onto the hydrophobic solid surface, are discussed. These two processes determine the effectiveness of the whole flotation process. The last chapter deals with bubble behaviour in aqueous solutions of simple alcohols.

The thesis summarises the basic problems that determine the efficiency of separation during plastic flotation. In the text, 15 works by the author are cited and refer to 81 core works in the field of plastics flotation and bubble-particle interactions. Links to the author's original work are highlighted in blue for clarity.

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1 Introduction

Particle-bubble interactions are a central issue in physico-chemical hydrodynamics, surface forces, multiphase reactors, and the dynamics of wetting films and adsorption at liquid interfaces. The mechanisms of bubble-particle interactions also control the selectivity and efficiency of the flotation process^[1]. This process is based on the ability of some solids to remain attached to the gas-liquid interface. Particles of such a solid then agglomerate with bubbles and are floated to the liquid surface, from which they can be easily separated. The flotation was originally used for the separation of coal or mineral particles from mined ore deposits. Owing to its simplicity and high efficiency, the flotation is nowadays also used for separation of oil sands, print inks in paper-recycling, waste water treatment, and also for separation of various plastic materials [2-5]. Plastics are extremely versatile materials and they are used for medicinal purposes, in everyday products including packaging for food and other goods, in the automotive industry, and in sports equipment and safety equipment like helmets or fire suits. In 2017, almost 40% of plastic was used in packaging, 20% in building and construction industry, 10% in automotive industry, and 6% in electrics and electronics [6]. The high demand for plastics means a high production rate with an estimated 60 million tonnes being produced in 2016 in the EU-27 alone while simultaneously producing a high level of waste. The European plastics industry had a turnover of more than 350 billion euros in 2017 and the European plastics industry had a trade balance of over 15 billion euros. In 2016, more than 8.4 million tonnes of plastic waste were collected to be recycled inside or outside the EU. By 2020, the EU-27 will have set a target of having zero plastics dumped in landfills. This target was set because plastic products at the end of their life are too valuable to discard since they can be re-formed into their original state, utilised to generate heat and power from combined heat and power plants, or used to bolster plastic supplies.

Of the four stages in plastic recycling: collection, separation, processing/manufacturing and marketing, separation is considered to be the most important as only the highest quality resins can be used for preparing plastic or chemical products. The EU has invested in developing new methods for the separation of plastics after collection, including smart and green interfaces, to help reach its goal. This method utilises flotation to separate the plastics, an already proven efficient separation method in mineral processing where the attachment of bubbles increases the floatation of some materials while depressing others allowing separation to occur. This habilitation thesis summarises approximately fifteen years of my work on bubble behaviour and bubble-particle interactions in flotation, focusing on the flotation of plastics. This thesis is divided into three major chapters. The first one describes the basic principles of plastics flotation including processes and chemicals used during the froth flotation process. In the end of the chapter, our contribution dealing with polystyrene flotability and wettability is included. The second chapter is the basis of my scientific work on the field of bubble-particle interactions in the flotation process. The basic principles and also differences of mineral and plastic flotation are compared in the beginning. Then I describe the collision of a spherical bubble with a falling spherical particle and the attachment of the bubble onto the hydrophobic solid surface. These two steps determine the effectiveness of the whole flotation process. The last chapter deals with bubble behaviour in aqueous solutions of simple alcohols.

2 Basic principles of plastic flotation

The application of flotation for the separation of plastic mixtures is relatively new. The earliest publications on this subject date back to the late seventies and originate from Japanese authors. The idea to apply the flotation technique to plastic separation was a logical step as ore flotation research has demonstrated that the surface properties of different materials can be altered selectively by surfactant adsorption [2]. Plastic recycling requires a previous separation between plastics and other constituents, and also between different polymer types, in order to achieve a good recycled plastic quality since most plastic types are not compatible with each other due to the immiscibility at the molecular level, which can cause serious processing problems and lowers the product quality[5]. As is currently known, it is too difficult to separate mixed plastic with slight differences in density by gravity separation, as well as to separate mixed plastic waste with slight differences in charge by the electrostatic technique. Flotation separation is based upon selective attachment of bubble on the particles to be separated, which requires a sufficient difference in the wettability of the particle surface. Plastics are hydrophobic by nature, therefore, the surface of one or more types should become hydrophilic while the others are kept hydrophobic. Flotation reagents can be divided into depressants, frothers, and collectors. In mineral flotation, low-molecular-weight surfactants, i.e., collectors, are usually used to render the valuable minerals hydrophobic, while high-molecular-weight polymers, called depressants, are used to render the undesired particles hydrophilic. In plastic flotation, mainly depressants are used [7, 8] due to the natural hydrophobicity of plastics. These compounds selectively wet plastics and thus they can be referred to as wetting agents for plastics flotation. Suitable wetting agents for plastics flotation are composed of molecular parts capable of adsorbing on plastic surface and molecular groups that render plastic particles hydrophilic. A series of wetting agents suitable for plastics flotation were reported such as tannic acid [9, 10], methylcellulose [11], and lignosulfonates [8, 12, 13].

Frothers create conditions for froth formation. These surface-active compounds contain a polar group and a hydrocarbon radical capable of adsorbing in the air-water interface. Frothers are utilised to facilitate air dispersion into fine bubbles and to stabilise the froth where the separated particles are collected. Frothers also interact with other molecules adsorbed onto the solid surface. Good flotation frothers have branched hydrocarbon radicals and form loosely packed gaseous films at the liquid/gas interface. Their hydrophile-lipophile properties must be properly balanced and for most good frothers, the HLB values are close to 6. This allows them to co-operate actively with the adsorbed collector in the moment of particle-bubble attachment. Increasing molecular weight at roughly the same HLB values makes frothers more powerful while those with lower molecular weight are more selective [14, 15]. The most well-known surfactants are MIBC (methyl isobutyl carbinol), terpineol (pine oil), Tritons, and the set of Dowfroths.

The earliest studies focused on testing reagents used in mineral and coal flotation. The majority of recycling processes start with size reduction followed by sink-float separation (density separation) to separate the lighter components, such as polyolefins (PP and PE) and foamed resins (PUR and expanded PS), from heavier plastics (ABS, PS, PET, PVC and PC etc.), and froth flotation is obviously suitable for separation of heavier plastics. The survey of results of separation for two-component mixtures is listed in Table 1. All mentioned authors, using different equipment and chemical environments, attained satisfactory results.

Authors	Reagents	Plastics		Recovery (wt. %)	
		Float	Non-float	Float	Non-float
Wang [12]	Tannic acid	PS	PET	98.60	94.60
		PC	PET	95.83	92.24
		PS	PC	97.08	94.44
		PET	PVC	98.63	95.73
		PS	PVC	98.88	95.30
		PC	PVC	96.94	94.86
	Lignin sulfonate	PET	PVC	99.25	98.35
		PS	PVC	96.71	98.15
		PC	PVC	98.09	97.21
	Methylcellulose	PET	PVC	96.72	93.90
		PS	PVC	96.62	93.71
		PC	PVC	91.98	93.13
	Triton X-100	PET	PVC	59.88	94.38
		PS	PVC	64.75	93.63
		PC	PVC	58.25	93.13
Pongstabodee [8]	Calcium lignosulfonate	PVC	PET	98.7	90.6
		PS	ABS	99.0	96.3
Marques [16]	Calcium lignosulfonate	PVC	PET	98.9	99.3
Singh [13]	Sodium lignin sulfonate	POM	PVC	95.0	97.0
	Sorbitan monolaurate	POM	PVC	80.0	95.0
Valdez [17]	Aeromine 3037	D-Nylon	Z-Nylon	99.0	98.5
	Aeromine 3037	ABS	Z-Nylon	96.6	89.0
Abbasi [9]	Tannic acid	PVC	PET	91.89	96.51
Shibata [10]	Lignin sulfonate	PC	PVC	74.0	99.6
		POM	PVC	96.7	90.2
		PPE	PVC	87.4	95.0
	Saponin	POM	PC	99.5	86.3
	Tannic acid	PPE	PC	85.5	99.0
	Sorbitan	PPE	POM	73.4	98.0

Table 1.Flotation separation of plastic mixtures [7]

In the following years, a number of articles have been published, whose authors try to separate multi-component mixtures [8, 10, 18]. For example, Pongstabodee [8] designed a process, enabling the three-stage separation method for the six mixed-plastic waste (HDPE, PP, PVC, PS, PET and ABS). Complete separation of HDPE from PP is achieved by a sink–float method with 50% v/v ethyl alcohol. Success in the separation of the PS/ABS mixture from the PET/PVC mixture is obtained by a sink–float method with 30% w/v calcium chloride. The separation of PET and PVC by selective flotation is achieved when using 500 mg/l calcium

lignosulfonate as a wetting agent, 0.01 ppm MIBC as a frother, and 0.1 mg/l CaCl₂ at pH = 11. To be successful in the separation of ABS from PS, 200 mg/l calcium lignosulfonate is used as a wetting agent and 0.1 mg/l CaCl₂ at pH = 7 is used as a flotation solution. This process is illustrated in Fig. 1.



Fig. 1 Scheme of the plastic recovery process by combination of sink–float method (gravity separation) and selective flotation technique [8].

In our research group, we studied the mutual coherence between the flotability and wettability of plastics (specifically polystyrene) at different concentrations of flotation agents [19]. We measured the surface tension, wettability and flotation recovery for four flotation agents. The results are given in Fig. 2. Terpineol, as the representative of the simplest type of frothers, does not affect the polystyrene wettability and its presence especially influences the properties of the flotation solution. It is used for the production of stable foam. Polyethylene glycol dodecyl ether, formally assigned to frothers due to high surface activity, considerably

enhances the wettability of polystyrene and above the concentration 60 mg/l decreases the flotability. The addition both of calcium lignosulfonate and tannic acid leads to considerable decrease of the flotability. In case of calcium lignosulfonate, the flotation recovery decreases significantly at low concentration, while in case of tannic acid it falls down with increasing concentration almost linearly. We proposed that the adsorption mechanisms of tannic acid and calcium lignosulfonate were different. We concluded that macromolecular wetting agents of the polyelectrolyte type adsorb more quickly on polymers that do not contain oxygen molecules in their structures and the non-ionic macromolecular wetting agents are more easily bound by polymers containing oxygen molecules.



Fig. 2. The concentration dependence of surface tension, wettability, and flotation recovery of polystyrene for the flotation agents terpineol, polyethylene glycol dodecyl ether, calcium lignosulfonate, and tannic acid.

3 The collision and adhesion process during the bubble-particle interaction

For the efficient bubble-particle capture, a sufficiently close encounter is required. The process is initially controlled by the hydrodynamics governing the bubble-particle approach in the liquid phase. As the particle and bubble come closer, the influence of intermolecular and interfacial forces increases. The liquid film between the bubble and particle surfaces begins to drain away, causing the film to rupture. The three-phase (air-liquid-particle) contact line becomes larger until a stable wetting perimeter is established and, at this point, a stable bubble-particle aggregate is formed. This bubble-particle interaction process is usually described as consisting of a sequence of three discrete steps [20-24]:

(i) collision - approach of the bubble and the particle to the contact distance;

(ii) attachment - adhesion of the particle to the bubble surface when the particle is smaller than the bubble; or adhesion of the bubble to the particle surface when the bubble is smaller than the particle. The attachment process begins with the drainage and rupture of the liquid film, and continues with contact line movement;

(iii) stability - detachment of the bubble from the particle surface occurs when the bubbleparticle aggregate is unstable.

The flotation overall probability (better efficiency) E of particle collection by a bubble can be represented by using the three probability terms:

$$E = E_c \cdot E_a \cdot E_d \,. \tag{1}$$

where E_c is the efficiency of collision between the particle and the bubble, E_a is the efficiency of adhesion after collision and E_d is the probability of maintaining the adhesion (or detachment)[25]. The collision and attachment processes will be described in the following text separately.

The bubble behaviour and also bubble-particle interactions are strongly influenced by the presence of surface active agents (surfactants). According to their structure, surfactants are amphipathic organic compounds that are composed of both a hydrophobic and hydrophilic section. Surfactants can be grouped into one of the following categories depending on the charge group on the head [26]: anionic, cationic, non-ionic, and zwitterion. In water, surfactants have two options to ensure each section interacts with its favoured environment. Firstly, it can arrange

itself so that the hydrophobic head is above the water's surface while the hydrophilic head is still submerged. Secondly, they can arrange into micelles, where the molecules form aggregates so that the head is exposed to water while the tail points towards the centre of the aggregate. The critical micelle concentration (CMC) is the concentration at which micelles form and any surfactant molecules that are subsequently added will join on to the micelles. In solutions of surfactants, the surface tension changes over time. A freshly formed liquid-gas interface has a surface tension very close to that of a solvent. Over a period of time, surface-active molecules adsorb onto the interface. The surface tension decays to its equilibrium value and this period of time can range from milliseconds to days depending on the surfactant type and concentration [27].

The surfactants in the bulk phase accumulate on the bubble surface due to their surfaceactive nature. These are then swept to the rear of the rising bubble due to the relative motion between the bubble and liquid phase, forming an inhomogeneous interfacial composition. The interface remains almost surfactant-free close to the bubble front stagnation point and the surfactant contamination accumulates in the rear region. Therefore, a concentration gradient is observed between the front and rear, which must be balanced by a jump in the shear stress that opposes the counter-current flow and partially immobilises the rear surface. This phenomenon is known as the stagnant cap hypothesis and it has been generally accepted for explaining the behaviour of contaminated multiphase systems [28]. In pure liquids (e.g. in pure water), no contaminants adhere onto the interface, the interface remains "mobile" and the liquid therefore exerts very low shear on the bubble surface. The surfactant molecules adsorb at the interface and immobilise the bubble surface to some extent. The flow around such a bubble and also its drag are well approximated by the behaviour of a solid particle with no-slip boundary condition for the liquid flow [29]. We talk about "contaminated" bubbles with fully or partially immobile surface.

3.1 Collision process

For a bubble to capture a hydrophobic particle efficiently, they must first undergo a sufficiently close encounter. A number of excellent reviews on determining the collision efficiency in mineral flotation mostly consider the gravitational, inertial, and interception mechanisms [22, 24]. The collision efficiency E_c is given by:

$$E_{\rm c} = 1 - (1 - E_{\rm g})(1 - E_{\rm s})(1 - E_{\rm i}).$$
⁽²⁾

Here, E_g , E_s and E_i denote the efficiencies due to gravity, the interception mechanism, and inertia respectively. In the standard flotation process, the particles are usually much smaller than the bubbles (we refer to these size proportions briefly as mineral flotation thereinafter). Oppositely in the case of plastics flotation, the particles are of comparable or even bigger size than bubbles. When this small bubble-large particle interaction is considered, we can utilise a similar description [30]. The efficiency due to the bubble buoyancy E_b replaces the gravity mechanism, and the E_c relation can be rewritten as:

$$E_{\rm c} = 1 - (1 - E_{\rm b})(1 - E_{\rm s})(1 - E_{\rm i}).$$
(3)

The importance of individual efficiencies will be discussed later. The typical scheme of bubbleparticle interaction in mineral flotation is illustrated in Fig. 3A. Bubble-particle interaction in plastics flotation, in which the particle is larger than the bubble, is described in Fig. 3B [30].



Fig. 3: Scheme of bubble–particle interaction process. A – single rising bubble and small falling particle; B – small rising bubble and large particle. Grazing trajectory with radius R_c , maximum initial angle $\varphi_{0,max}$ and maximum collision angle $\varphi_{c,max}$ are denoted.

The critical trajectory, known as the grazing trajectory, distinguishes the trajectories of particles that encounter the bubble from the trajectories of those that do not, and is characterised by the critical radius R_c and the critical collision angle $\varphi_{c,max}$. The polar angle φ is measured at the bubble centre and from the front stagnation bubble point.

The flotation efficiency is defined as the ratio of the number of colliding particles to the total number of particles in the swept volume [22, 31]. The collision efficiency E_c can be defined analogously as the ratio of the number of bubbles colliding with the particle to the number of bubbles that would collide if their trajectories were not deflected by the flow around the particle (see Fig. 3). Similar to the case of mineral flotation [22, 32], this efficiency can be determined from the bubble grazing trajectory (with initial angle $\varphi_{0,max}$), which distinguishes the trajectories of bubbles that encounter the particle surface from those that do not. Based on a simple geometric interpretation of the grazing trajectory, one can obtain the following simple relation [22]:

$$E_{\rm c} = \left(\frac{R_c}{R_p + R_b}\right)^2 = \sin^2(\varphi_{0,\rm max}).$$
(4)

Here $\varphi_{0,\text{max}}$ is the initial angle corresponding to the grazing trajectory [33, 34].

In our research group, we focused on the determination of collision efficiency from experimental data and we proposed a new theoretical model [34, 35]. The bubble is considered spherical and can be either clean (with mobile interface, pure liquids) or contaminated (immobile interface, aqueous solutions with surface-active agents). The particle is also spherical and moves vertically downward with a steady velocity. The model assumes potential flow around the spherical particle ([36]; $Re_p = \rho U_p D_p / \eta >> 1$) and balances forces acting on the bubble, leading to a differential equation for its motion [29]. Here, the buoyancy (F_b), drag (F_d), added-mass force (F_{am}), inertial force (F_I) and lift due to the flow restriction by the particle (F_L) were considered. The bubble motion was finally described by a system of equations

$$\frac{d}{dt} \begin{pmatrix} r_{b} \\ \theta_{b} \\ \frac{dP_{b}}{dt} \\ \frac{d\theta_{b}}{dt} \end{pmatrix} = \begin{pmatrix} \frac{dr_{b}}{dt} \\ \frac{d\theta_{b}}{dt} \\ r_{b} \left(\frac{d\theta_{b}}{d\tau} \right)^{2} + \frac{F_{b,r} + F_{d,r} + F_{aml,r} + F_{amp,r} + F_{I,r} + F_{L,r}}{V_{b} \left(C_{M,r} \rho + \rho_{g} \right)} \\ - \frac{2}{r_{b}} \left(\frac{dr_{b}}{d\tau} \right) \left(\frac{d\theta_{b}}{d\tau} \right) + \frac{F_{b,\theta} + F_{d,\theta} + F_{aml,\theta} + F_{amp,\theta} + F_{I,\theta} + F_{L,\theta}}{V_{b} \left(C_{M,\theta} \rho + \rho_{g} \right)} ,$$
(5)

where the bubble position was characterised by spherical coordinates r_b and θ_b .

The experimental bubble trajectory was described using the bubble initial horizontal position x_0 and its position x_{col} at the collision. On the condition that the frame of reference

moves together with the particle and its origin is fixed in the particle's centre, the horizontal position of the bubble centre in its initial position (sufficiently distant from the particle) can be defined as x_0 and simultaneously the position of the bubble centre at the collision point can be characterised by its horizontal position, x_{col} . It was observed that the collision position increases almost linearly with the initial position, thus the parameter k characterises the bubble deviation from its vertical path caused by the flow around the particle. The linear dependence was confirmed both experimentally and theoretically [34]. Based on a simple geometric interpretation of the grazing trajectory, one obtains for the bubble-particle collision efficiency $E_c \approx 1/k^2$. If the parameter k is plotted against the ratio of terminal bubble and particle velocity U_b/U_p we obtain a single master curve. It demonstrates the importance of the velocity ratio as the dimensionless parameter controlling the collision process between small bubbles and large particles [34]. This linear dependence is consistent with the Flint-Howarth buoyancy model [37]

$$E_{\rm b} = \frac{U_{\rm b}}{U_{\rm b} + U_{\rm p}}.\tag{6}$$

The dependence of the collision efficiency E_c on the ratio U_b/U_p is illustrated in Fig. 4. The experimental efficiencies are depicted as circles and rhombi. The efficiencies calculated using the theoretical model (eq. 6) are illustrated with squares. The efficiencies calculated using equation 3 are illustrated with crosses; details are given in [33]. The efficiency calculated using the Flint–Howarth buoyancy model is shown as the full black line. It is obvious that the Flint–Howarth buoyancy model underestimates efficiencies for lower values U_b/U_p . Therefore, we included the influence of interception and inertia mechanisms and we proposed the following equation [33]:

$$E_{c} = \frac{U_{b}/U_{p}}{1.02568 \ U_{b}/U_{p} + 0.74057} \,. \tag{7}$$

This equation and all above mentioned conclusions are valid for bubbles both with mobile and immobile surface, where the immobile surface is considered in systems with surface active agents. The surface immobilisation leads to the increase of drag and thus also to the bubble rise velocity decrease. The bubble rise velocity drops by roughly half. The bubble Reynolds numbers ranged from 5 to 180 and particle Reynolds numbers ranged from 35 to 1400.



Fig. 4 Dependence of the collision efficiency E_c on the relative velocity ratio U_b/U_p .

The overall efficiency in plastic flotation is thus controlled mostly by the buoyancy of the bubbles and only partially by the interception mechanism and inertial effects. In the mineral flotation, the situation is the opposite and the interception mechanism or inertial effects are crucial. Particle inertia is important for heavy and/or large particles and becomes dominant for Stokes number greater than unity. For a smaller Stokes number, the interception mechanism predominates. We confirmed the view that the inverted size proportion changes the mechanics of bubble-particle interaction [38].

3.2 Attachment process

The bubble adhesion onto the hydrophobic particle and the stability of created unit are the most important parts for the determination of the effectiveness of the whole separation process in flotation. It is commonly accepted that the bubble attachment consists of two terms [21, 39]:

(i) thinning of liquid film to a critical thickness where the rupture of the liquid film begins; and

(ii) expansion of the three-phase contact line to form a stable wetting perimeter. This perimeter is usually named as the three-phase contact line (TPC line).

When the bubble and the particle are sufficiently close together, a liquid interface film is formed between the bubble and the particle surface. The rate of the film depletion (often referred to as film drainage rate) is limited by the liquid viscosity at the beginning of the process, reaching its critical thickness. At this point, the rate starts to be influenced by the intermolecular forces acting between the molecules of the liquid and the solid particle. Initially it was assumed that the rupture of the liquid film is connected with the density fluctuations and the TPC contact arises from a hole of a certain diameter in the intervening liquid film [22, 40, 41]. Nowadays, the surface hydrophobicity or hydrophilicity is considered to be a major factor influencing liquid film rupture. Whereas in the case of hydrophilic surfaces, the intermolecular forces stabilise the liquid interface film so that the bubble never adheres to the solid surface, in the case of hydrophobic surfaces, the forces act to destabilise the film and eventually break it to form the three-phase contact line [42-45]. The liquid interface film ruptures in the case of highly hydrophobic solid surfaces, but the time of depletion depends on the stability of the film formed, its drainage kinetics and the critical thickness of its rupture [46, 47]. Generally, the more hydrophobic the surface is, the less stable the interface film is. Since the hydrophobic surfaces show a high affinity to air, the roughness of the solid surface plays an important role as well because the surface cavities or scratches can entrap air in the form of micro- or nano-bubbles. Zawala [46] suggested that the presence of air facilitates the film rupture due to the low stability of the local liquid films between the micro- or nano-bubbles and the colliding bubble. The three-phase contact (TPC) line in pure water is then formed as a result of coalescence between submicroscopic bubbles already attached to the hydrophobic surfaces and the colliding bubble.

After the rupture of the interface film, the liquid phase begins to retreat from the solid surface due to an uneven distribution of the liquid-gas interfacial tension. The movement of the three-phase contact line is involved in both the wetting and dewetting mechanisms. Dewetting is applied in the case of bubble adhesion on a solid particle, while wetting occurs during liquid drop spreading on a solid surface. The contact line movement is driven by fluid dynamics and molecular interactions of the contacting phases. Surface tension and inertial and viscous forces influence the expansion of the TPC line.

In our research group, we focused on the detailed description of the TPC enlargement [27, 48-52] and on the influence of different types of surfactants [53, 54]. The second topic is described in the next chapter. The dynamic process of either wetting or dewetting can be described by the velocity of the contact line expansion U which is defined as

$$U = \frac{dR_{TPC}}{dt}.$$
(8)

Here, R_{TPC} is the diameter of the three-phase contact line and t is time. Several theoretical models have been developed to describe the TPC line expansion, relating the velocity dependence on dynamic contact angle to measurable properties such as surface and interfacial tension, liquid viscosity and static contact angle. Historically, the two main approaches are the hydrodynamic and molecular-kinetic models. An alternative view is the combined model, which applies both surface and hydrodynamic factors [55-57]. Cox [58] established the basics of the hydrodynamic model for the wetting mechanism. It suggests that the process is dominated by the fluid viscous dissipation. Thus, the bulk viscous friction is the main resistance force for the TPC line contact motion [57]. The main deficiency of this model is the description of the fluid motion very near to the contact line. The slip length of the nanometre scale was introduced to describe the unique hydrodynamic mechanisms acting in close proximity of the contact line [55]. Use of the hydrodynamic theory has been suggested for wetting mechanism at low contact velocities [57]. The second theoretical model is the molecular-kinetic model which eliminates the viscous dissipation but includes the solid surface characteristics. The theory is based on a statistical treatment of the transport mechanism of molecules and ions. This model assumes the energy dissipation to occur only at the moving contact line, where adsorption and desorption processes occur. The movement of the TPC line is ruled by the statistic kinetics of molecular events arising at the adsorption sites of the solid surface [55]. The most common approach to the molecularkinetic model is the one proposed by Blake and Haynes [59], which is commonly applied to dynamic wetting. Since it was shown that the two mentioned models do not fit the entire velocity range of experimental data, a combined molecular-hydrodynamic approach has been proposed [55, 57, 60]. The dewetting hydrodynamics is used to describe the effect of fluid flow on the interface deformation far from the three-phase contact line and the molecular kinetics is used to describe the dewetting close to the contact line. Recently, Fetzer and Ralston [61] concluded that the molecular displacements are not caused by adsorption or desorption events but rather by the nanometre-scale surface heterogeneity (chemical or topographical), which influences the contact line motion in a low-velocity regime.

All abovementioned models describing TPC line extension are based on similar principles that the liquid film break occurs on the bubble symmetry axis, the position of the bubble's centre of gravity position is on the vertical axis of symmetry, and the radius of the TPC line gradually increases as the velocity of the TPC line expansion decreases. These assumptions have not yet been experimentally verified. Our project was thus focused firstly on the detailed experimental study of bubble adhesion on a hydrophobic solid surface and later, with the cooperation of our polish partners, on the numerical simulations of kinetics of the TPC line expansion. We used the high-speed camera in a side position in high resolution and capture frequency 16000 fps in order to precisely capture the bubble motion and shape oscillation during the adhesion. A series of photos illustrating the adhesion of the bubble onto the hydrophobic solid surface in pure water is given in Figure 5.



Fig. 5. A series of photos illustrating the adhesion of the bubble ($D_b = 0.705 \text{ mm}$) onto the hydrophobic solid surface in pure water. The time interval between individual shots is 0.0625 ms.

The bubble adhesion is much slower in solutions of surface active agent. An example is illustrated in Figure 6. The sequence of photos illustrates the bubble ($D_b = 0.712$ mm) adhesion onto the solid surface in an aqueous solution of anionic surfactant sodium dodecyl sulphate SDS.



Fig. 6. Sequence of photos illustrating a course and outcome of the bubble ($D_b = 0.712 \text{ mm}$) adhesion onto the solid surface in aqueous solution of SDS at concentration $2 \times 10^{-2} \text{ mol/l}$. The time interval between individual points is 0.25 ms. The final image represents equilibrium at t = 25 ms.

Our most important conclusions can be summarised in the following points [27, 49]:

i) The rupture of a liquid film is not symmetrical with respect to the vertical axis of the bubble symmetry. This finding is in accordance with the conclusion of Chan [62], who proved that the liquid film becomes the thinnest close to the apparent contact line.

ii) The asymmetry of the TPC line formation leads to bubble surface oscillations and asymmetry in dynamic contact angles. In case of completely mobile liquid/gas interface, corresponding to pure water, the uneven motion of the TPC line causes the change of boundary conditions and characteristic bubble shape oscillations were observed during the TPC line formation and expansion. Similar linear oscillations and irrotational flow during the bubble contact with the solid surface were described by Vejražka [63]. The TPC expansion velocity vs time curve exhibits a characteristic peak around 1 - 2 milliseconds after the liquid film rupture. We proved that this characteristic peak has the hydrodynamic origin and is associated with a local

increase of total kinetic energy of the system, resulting from quite violent bubble shape pulsations. The time dependence of the expansion velocity U in pure water is shown in Figure 7A.

iii) In surfactant solutions, the effect of the liquid/gas interface immobilisation is very significant, because the bubble shape pulsations are damped and kinetic energy changes were smaller and smoother. Also the velocity of TPC expansion is significantly slower. The forces of the surface tension gradient overcome the viscous forces and the hydrodynamic model is not able to explain the non-monotonic curve of the expansion velocity profile in surfactant solutions. Also the molecular-kinetic model fails. We suppose that the arising Marangoni stresses should be taken into account because the expansion velocity increases in the first moments of the TPC line expansion. The time dependence of the expansion velocity *U* in an aqueous solution of SDS at concentration 2×10^{-2} mol/l is shown in Figure 7B.



Fig.7. Average TPC expansion velocity for bubbles with diameters 0.70 mm, 0.74 mm and 0.85 mm in pure water (detail A) and for bubbles with diameters 0.71 mm, 0.74 mm and 0.87 mm in aqueous solution of SDS at concentration 2×10^{-2} mol/l (detail B).

3.3 Bubble adhesion onto the solid surface in aqueous solutions of surface active agents

In this section, I would like to mention in more detail the influence of the surfactant type and its purity on the dynamics of the bubble adhesion process. The stability and velocity of bubble attachment determines the effectiveness of the whole separation process in flotation. Thus both fast adhesion process and high contact angles are required. The TPC line dynamics could be influenced by the surfactant adhesion on solid-liquid, solid-gas, and liquid-gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration.

Nonionic surfactants are electrically neutral. Some of the most important advantages can include a significantly lower sensitivity to the presence of electrolytes in the system, a reduced effect of solution pH, and the synthetic flexibility of the ability to design the required degree of solubility into the molecule by the careful control of the size of the hydrophilic group. This group encompasses a large number of synthetic chemicals of varied types and structures. In our study we used three non-ionic surface-active agents [54]:

(i) Terpineol; a monoterpene alcohol which is often used as a flotation frother,

(ii) Triton X-100, which has a hydrophilic polyethylene oxide chain (on average it has 9.5 ethylene oxide units) and an aromatic hydrocarbon group. Triton is used as a detergent.

(iii) pentaethylene glycol monododecyl ether (referred to as $C_{12}E_5$), which is formed by dodecanol hydrocarbon group and five repeat units of ethylene glycol.

The results for the bubble adhesion in water and solutions of surfactant are illustrated in Figure 8. The ratio of the diameter of the TPC line against bubble diameter D_{TPC}/D_b is plotted against time. For the stable bubble attachment, this ratio should be high and the attachment time should be quick. In pure liquids, the ratio should be independent of the bubble size.

We confirmed that the bubble adhesion is fast in solutions of such surfactants, whose hydrophobic and hydrophilic parts are small. Due to the immediate transport of molecules onto the liquid-gas interface the decrease of surface tension is fast and also the small molecules do not significantly hinder the TPC line expansion. Terpineol seems like a typical representative of such a substance. The bubble attachment is stable even in solutions with higher concentrations (with lower surface tension) and therefore Terpineol can be recommended as a suitable flotation agent.



Fig. 8. The ratio D_{TPC}/D_b for bubble adhesion in water and surfactant solutions.

In case of large or else complex molecules, an adsorption barrier preventing the monomer from adsorbing should be expected [64]. This barrier comes into existence in dilute solutions; then rises with increasing concentration and again changes close to the CMC concentration. The existence of such a barrier is often connected with some steric restraints on the molecule in the proximity of the interface because the molecules should be in the correct orientation. Unsuitable orientation could cause the molecule to diffuse back into the bulk rather than adsorbing. In accordance with this theory, we have shown that surfactants with long and flexible hydrophobic tails (pentaethylene glycol monododecyl ether, Triton X-100) exhibit slower and more complex behaviours. In general we can say that the bubble adhesion is very slow in solutions with surfactant concentrations, both the surfactant structure and bubble size play an important role. We assume the existence of adsorption barriers close to the interfaces which influence the surfactant motion. Molecules of pentaethylene glycol monododecyl ether are very long and could create certain small aggregates captured on the phase interface. The transport of such molecules is very low and thus, surprisingly, their influence on the velocity of TPC line expansion could be very low. Similar phenomena were not observed for Triton solutions. The explanation of the observed complex behaviour is far more speculative; but it is certain that non-ionic surfactants with long hydrophobic chains are unsuitable as flotation agents.

Ionic surfactants are the largest group of surfactants used today with more than 75% of total worldwide consumption. Within the anionic group there are sulphate esters, sulfonic acid salts, carboxylate soaps and detergents, and phosphoric acid esters. The sulphate ester family is one of the most significant due to the sodium dodecyl sulphate (SDS); the most widely studied and used surfactant. Cationic surfactants are important in cosmetics as antiseptic agents, fungicides, germicides, fabric softeners, and hair conditioners. The sources of hydrophobic groups are mostly natural fatty acids or derivatives from petrochemical compounds; in all cases they contain nitrogen. One of the most studied cationic surfactants is dodecyltrimethylammonium bromide (DTAB). The ionic surfactants used both in industrial applications and in scientific studies, as a rule, contain some admixtures of non-ionic surfactants or other contaminants. The presence of contaminants has a dramatic effect not only on the surface properties [65], but also on shear viscosity and foam stability [28, 66, 67]. The co-adsorption leads to a significant decrease of the interfacial tensions, which influences the final contact angle. Thereby the bubble attachment efficiency lowers, which has a significant impact on the entire flotation process[53]. Dodecanol is the most important contaminant and is one of the most difficult to remove [68, 69]. Even at impurity levels below 0.1%, dodecanol reduces the surface tension and leads to the wellknown minimum below the critical micelle concentration.

In our research group, we have analysed the influence of possible contaminants of ionic surfactants on the dynamics of bubble adhesion onto a hydrophobic surface [53]. Experiments were carried out in pure and technical grade solutions of cationic *n*-dodecyltrimethylammonium bromide (DTAB) and anionic sodium dodecyl sulphate (SDS). For pure, mono-component ionic surfactants, we observed a linear dependence between the surfactant concentration and bubble adhesion efficiency, which could be expressed by surface tension, bubble contact angle, or the TPC line diameter. The results are illustrated in Figures 9 and 10 in details A. The surfactants with lower purity are usually used both in industrial applications and experiments at the pilot level. Their common contaminant is dodecanol. On the basis of the measurement of dynamic

surface tension, we found that its concentration in the monolayer reaches a maximum below the CMC and in case of bubble lifetimes longer than few seconds, the contaminants are more surface active than the main component. The contaminants generally decrease the bubble adhesion efficiency when compared with the mono-surfactant solution. Their influence is crucial in the range 0.8 CMC to 1 CMC. Here, the surface tension is decreased below the value typical for CMC, the bubble contact angles are likewise lower and the velocity of TPC line expansion slows significantly. It may even happen that the capture of bubbles is avoided (see Fig. 9A).



Fig. 9. The ratio D_{TPC}/D_b for bubble adhesion in SDS solutions. Detail A gives data for high purity SDS and detail B gives data for low purity sample.



Fig. 10. The ratio D_{TPC}/D_b for bubble adhesion in DTAB solutions. Detail A gives data for high purity DTAB and detail B gives data for low purity sample.

4 Bubble behaviour in aqueous solutions of simple alcohols

The aqueous solutions of simple alcohols have been thoroughly investigated for decades by biologists, chemists, and engineers due to their exceptional practical importance in many industrial, biological, and pharmaceutical applications. Here, they are used most often as cosolvents and co-surfactants. Ethanol, for example, is used as a density-lowering agent [8] or, in low concentrations, as a surfactant during the flotation process [70-73]. The aqueous solutions of methanol, ethanol, and propanol exhibit atypical physicochemical properties. Relatively wellknown is the volume reduction of the mixture in comparison to the volume in the "pure" alcohol or water states. From the chemical-engineering point of view, the maximum in viscositycomposition dependence and lower wettability in comparison to common liquids have a much greater significance [74, 75]. Also other thermodynamic and transport properties, such as volume reduction of mixture, diffusion coefficient, surface tension, heat capacity, etc., vary significantly relative to the "pure" alcohol or water states as a result [76]. These peculiar properties result from the formation of organised microstructures in the non-ideal mixture at a molecular level [77, 78] because it leads to the formation of various microscopic pseudo-clathrate chainlike structures or even micelle like clusters in the surrounding water. The existence of this molecular organisation has been proved by several independent methods [77]. These structures can have an effect on the interfacial properties of liquid mixtures and may cause unpredictable anomalies in the behaviour of systems where the surface phenomena play an important role. The typical examples are the motion of dispersed fluid particles (bubbles, drops) through the carrying bulk liquid, hydrodynamic interactions between such particles (coalescence and breakup), and the behaviour of fluid particles at rigid surfaces (adhesion). Such situations commonly occur in many important technological processes and equipment (fermenters, adsorption columns, waste water treatment, flotation, etc.), which presents strong motivation for the research.

If we look deeper into the molecular structure, we can recognise different regions which characterise the solution structure. At very low alcohol concentrations, water molecules completely surround the alkyl groups and undergo hydrophobic hydration. The formation of alcohol-water clusters is observed within a narrow range of concentration and above this "critical" concentration the number of clusters grows with increasing alcohol concentration. Takamuku [79, 80] investigated the microscopic structure using the method of X-ray diffraction

and mass spectroscopy and observed a structural change from a tetrahedral-like water network to chains of hydrogen bonded alcohol molecules occurring at methanol mole fraction of $x_M \approx 0.3$, ethanol mole fraction of $x_E \approx 0.2$ and at propanol mole fraction $x_P \approx 0.1$. Chodzinska [76] determined critical concentrations on the basis of the surface tension isotherms (the values of the mole fraction corresponding to the aggregation of methanol, ethanol, and propanol are equal to 0.28, 0.17, and 0.07 respectively), while Takaizumi [80, 81] used the differential scanning calorimetry (molar fractions $x_M = 0.3$, $x_E = 0.17$ and $x_P = 0.1$). Finally, in the alcohol-rich region, the water behaves as a solvent in the alcohol solution as there are no longer enough water molecules to form the strong cluster networks.

In our research group, we explore the consequences of the atypical properties of wateralcohol binary solutions on the behaviour of dispersed multiphase systems. Using the high-speed video camera, the terminal velocities of spherical bubbles were determined in water-ethanol and water-propanol mixtures covering the whole range of concentration, from pure water to pure alcohols. The corresponding drag coefficients were calculated and used to assess the mobility state of the bubbles' interface. As an example, results for a bubble having diameter 0.6 mm are illustrated in the Figure 11.



Fig. 11. *Terminal bubble velocity as a function of ethanol (left) and propanol (right) concentration. The full line* (—) *represents the calculated velocity for mobile bubble surface. The dashed line* (--) *represents the calculated velocity for immobile bubble surface.*

In this picture, experimental terminal bubble velocity is plotted as a function of ethanol or propanol concentration. Limit values are curves for bubbles with mobile and immobile surfaces. The upper full line represents the calculated velocity for mobile bubble surface and the lower dashed line represents the calculated velocity for immobile (contaminated) bubble surface. A decrease in bubble velocity for the alcohol concentration of about 30% is due to the increase in viscosity. Firstly, a substantial decrease in terminal rise velocity with only a small addition of alcohol is visible. At a molar fraction of 0.01 for ethanol and 0.003 for propanol, the velocity observed was almost that predicted for a bubble with fully immobile interface. This is due to surfactant-like behaviour of the alcohol molecules, restricting the mobility of the surface and retarding the motion of the bubble. With increasing alcohol content, the velocity unexpectedly increases. For ethanol, this observation can be made between molar fractions of $0.05 \le x_E \le 0.10$. An even more pronounced trend was observed for propanol in the range $0.005 \le x_P \le 0.07$. Above molar concentrations of $x_E = 0.15$ and $x_P = 0.07$, the bubble velocity closely matches the predictions for a fully mobile bubble surface.

The behaviour across the full composition range is rather complex, with a clear gradual transition between a completely immobilised bubble surface at low concentrations and a fully mobilised surface at concentrations above the critical aggregation concentration. Based on the alcohol concentration we can divide the aqueous solution of simple alcohols into 3 regions [74]:

i) mixtures with very low alcohol content. At low concentrations ($x_E \le 0.01$, $x_P \le 0.005$), the mixtures behave as solutions containing surface active agents. Alcohol molecules that are present in the solution diffuse very quickly onto the phase interface and adsorb onto the surface of the bubble, thus increasing the shear stress and drag. The concentration of alcohol in the interface layer is higher than in bulk and thus the interface behaviour is changed. We can observe a significant decrease in surface tension, but the properties of the bulk liquid (density, viscosity) are still relatively consistent. The drag coefficient is well approximated by the behaviour of a solid particle with no-slip boundary condition for the liquid flow. Overall, it can be summarised that simple alcohols acting as surface active agents exhibit the maximum surface effect at very low concentrations. For propanol, we found this maximum between molar fractions of 0.001 to 0.005. For ethanol, the maximum was observed between molar fractions from 0.005 to 0.01.

ii) mixtures with medium alcohol content (0.01 $\le x_E \le$ 0.20, 0.005 $\le x_P \le$ 0.07). In this region, the behaviour of the mixture varies significantly with the changing alcohol concentration.

Micro-aggregates have not begun to form but the molecular bonds between alcohol and water are changing. The viscosity increases and also the concentration gradient reduces in conjunction with the gradient of surface tension. The surface tension gradient is balanced by the decreasing shear stress exerted on the bubble surface by the liquid. In summary, the desorption of alcohol molecules from the phase interface is facilitated, which in-turn reduces the drag force and subsequently causes an increase in terminal rising velocity. Due to the changing concentration and surface tension gradients, the drag coefficient decreases.

iii) mixtures with high alcohol content. Above $x_E \ge 0.20$ and $x_P \ge 0.07$, the properties of the mixtures are influenced by the existence of clusters or micro-aggregates. In this region, in which alcohol and water molecules form complete and stable clusters within the solution, the liquid flow exerts very low shear due to the minimal gradient of surface tension. The aqueous solutions of simple alcohols behave like pseudo-pure substances and the bubble surface is shown to be completely mobile.

5 Conclusions

This habilitation thesis introduces the reader into the world of bubble-particle interactions in the flotation of plastics. The worldwide high demand for plastics means a high production rate and, simultaneously, a high amount of waste. Nowadays, many researches are invested in developing new methods for the separation of waste plastics. One method for separation of plastics utilises flotation, an already proven efficient separation method in mineral processing. At present, the possibilities of separating individual types of plastics, as well as the mechanisms of interaction of bubbles and solids in flotation, are studied. This habilitation thesis reflects this trend to a large extent.

The first part of this thesis summarises the basic principles of flotation of plastic. The differences between mineral (classical) and plastic flotation are described and the utilisation of various flotation agents is discussed. The second part is focused on the bubble-particle interactions. The description of the collision process focuses in detail on the case of a falling spherical particle and a rising spherical bubble. It was proved that the collision efficiency in plastic flotation is controlled mostly by the buoyancy of the bubbles. Furthermore, adhesion of

the bubbles to the hydrophobic surface is studied because the plastics are also hydrophobic. This chapter is specifically focused on the influence of surface active agents on adhesion efficiency, with emphasis on the type and purity of these agents. The last part of the habilitation thesis is devoted to the dynamics of bubbles in solutions of simple alcohols, which show a number of atypical properties due to their organised molecular structure.

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The influence of flotation agent concentration on the wettability and flotability of polystyrene

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Abstract

The fundamental flotation process is the formation of a flocculant by air bubbles and solid particles in an aqueous solution. The behavior of plastic particles is significantly influenced by the wettability of the plastics. In this article the reciprocal relationship between the flotability and wettability of polystyrene was studied at different concentrations of flotation agents, particularly terpineol, polyethylene glycol dodecyl ether, tannic acid, and calcium lignosulfonate. The conclusions obtained demonstrate the dissimilar action of flotation depressants, what means different adhesion mechanisms on a plastic surface.

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Keywords: Plastics flotation; Contact angle; Surface tension; Polystyrene

1. Introduction

The study of fundamental impact of flotation agents began with the first flotation experiments in the 19th century. First mineral ores and coal were separated using flotation methods; in later decades waste water has been cleaned and mixtures of plastics have been separated using similar principles. The reagents employed in flotation are generally interfacial surface tension modifiers, surface chemistry modifiers, and flocculants. Usually they are classified under five headings: collectors (sometimes known as flotation promoters), frothers, modifiers, activators, and depressors [1]. In this article attention is paid to two basic types of agentsfrothers and depressors. Frothers are surface-active reagents that aid in the formation and stabilization of air-induced flotation froth. The commonly employed frothing agents are alcohols, which are only slightly soluble in water, and more modern frothers, which are generally varieties of polyethers or polyglycol ethers that are completely miscible with wa-

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ter. Collectors and also depressors, which are more specific, are reagents that coat or react with particle surfaces and make them water-repellent or attachable to air bubbles. Depressors assist in separation when the flotability of two or more substances is too similar for a particular collector to effect a separation and increase wettability of one type of the particles. We recognize inorganic and organic depressors; organic depressors are large molecules, usually with a molecular weight above 10,000. The natural products are generally polysaccharides, while new synthetic depressors include polyglycol ethers and polyphenols.

Macromolecular depressants are widely used for suppressing flotation of naturally hydrophobic materials. Due to the close analogy between naturally flotable minerals and plastics with regard to flotation, such reagents have been tested in flotation research. Polymers used in practical applications are mostly polydisperse. This reflects the flotation agent's being a mixture of polymer molecules of various chain lengths. It is presumed that longer chains will gradually displace shorter ones from the solid surface when the agent concentration is heightened, and thus the total number of long chains will increase. At a given concentration, preferably long chains will be on the surface while the short ones remain in solution [2]. Therefore, the depressor concentration plays a significant role in the flotation process.

2. Experimental materials and methods

2.1. Materials

The standard polystyrene (GP-PS) used for the experiments originated from the Stirol company (Ukraine) and was obtained from a local agent under the trademark Stirol 118. According to the manufacturer this material is free from additives and its melting index is 12 g/10 min. The particle diameter was about 4 mm and the density 993 kg/m³. For the measurement of surface tension and contact angles distilled water was used; for the measurement of flotation recovery and wettability tap water was used. pH was 7.2, conductivity 47.6 mS/m, and ionic strength 12.3 mmol/l.

The agents used for flotation experiments included the frothers terpineol and polyethylene glycol dodecyl ether (also called Brij 30) from the Fluka company and the wetting agents tannic acid and calcium lignosulfonate supplied by Penta Prague and Sigma-Aldrich, respectively. Their CAS numbers, molecular formulae, and molecular weights and the calcium concentration in calcium lignosulfonate are listed in Table 1.

2.2. Surface tension and contact angle measurements

The surface tensions of water and solutions of flotation agents were measured using the semistatic ring method. A LAUDA TD1 tensiometer with outer thermostating of the measuring vessel was used. During all experiments a constant temperature of 25 °C was maintained.

The contact angles were measured by a direct method, monitoring the drop profile on a smooth flat surface, represented here by a polystyrene foil. The method is based on the following principle: an illuminated drop, in particular its contact point with the solid surface, is monitored under a microscope with sufficient enlargement and scanned by a video camera and its signal is processed by a computer. The contact angles were evaluated by the Image Tool program. The PS-coated surfaces were prepared by a solvent-casting technique; the plastic granules were dissolved in chloroform and the solution was infused on a microscope glass. After chloroform had evaporated, a thin but very compact and even layer of plastics was formed.

2.3. Flotation experiments

The flotation experiments were performed on a laboratory flotator of Denver type with vessel content 1.4 L. The weight was always 100 g and tap water was used for the experiments. The flotation time was 10 min. The recovery at the end of a flotation test was determined by weighing the particles collected in the outgoing phase. The percentage recovery corresponds to the mean value of three tests.

3. Results and discussion

3.1. Surface tension

Initially the surface tensions of distilled and tap water were measured. For distilled water a value of 71.9 mN/m was obtained at 25 °C, which is in good agreement with the literature data (71.97 mN/m [3] and 72.1 mN/m [4]). The surface tension of tap water at the same temperature was 72.0 mN/m. From the above value it is obvious that only mineral substances without surfactants were dissolved in the tap water. Therefore, for surface tension and contact angle measurements, distilled water was used, and tap water was used for flotation experiments.

The concentration dependence of surface tension was measured in solutions of four flotation agents. In Table 2 results are shown as average values of three measurements. From these data it is obvious that the solutions of the frothers, in particular polyethylene glycol dodecyl ether, have the greatest influence on the value of the surface tension. Polyethylene glycol dodecyl ether, often used as a very strong surfactant, decreased the surface tension by more then 50%. On the other hand, the wetting agents do not change the surface tension of the solution, what corresponds to their physical nature.

3.2. Contact angles

In the presence of air bubbles the behavior of the plastic particles is significantly influenced by the wettability of the plastics. If a drop of liquid (water) is placed on a smooth solid surface it takes a specific shape due to solid–liquid interactions. This configuration has minimum free energy and

Table 1

CAS number, molecular formula, and	a molecular weight of flotation	1 agents
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	CAS number	Molecular formula	Molecular weight (g/mol)	Notes
Calcium lignosulfonate	8061-52-7	C ₁₁₅ H ₁₃₂ O ₄₀ SCa (approx.)	2225 (aver.)	5% Ca (wt)
Terpineol	8006-39-1	C ₁₀ H ₁₈ O	154.25	
Tannic acid	1401-55-4	C ₇₆ H ₅₂ O ₄₆	1701.23	
Polyethylene glycol dodecyl ether	9002-92-0	$C_{20}H_{42}O_5$	362 (aver.)	

Table 2					
Surface tensions of	of solutions of flotation	n agents (temperature	25 °C) and their	concentration depende	nce

		Calcium l	ignosulfonate			
Concentration (mg/l)	10.0	20.0	30.0	50.0	70.0	100.0
Surface tension (mN/m)	71.2	71.0	71.2	71.5	71.5	71.6
		Ter	rpineol			
Concentration (mg/l)	19.8	29.2	31.6	50.0	78.4	
Surface tension (mN/m)	71.1	69.8	69.9	69.1	68.0	
		Tan	nic acid			
Concentration (mg/l)	10.0	20.0	50.0	70.0		
Surface tension (mN/m)	71.9	71.7	71.6	71.6		
		Polyethylene g	lycol dodecyl ether			
Concentration (mg/l)	10.0	21.2	30.6	50.0	70.0	100.0
Surface tension (mN/m)	36.4	31.6	30.7	30.2	29.0	28.3

Table 3

Experimental contact angles for solutions of flotation agents at various concentrations

Flotation agent	Contact angle (°)							
	7.9 mg/l	20 mg/l	30 mg/l	50 mg/l	100 mg/l	200 mg/l		
Calcium lignosulfonate		82		80	77	77		
Tannic acid				81	79	79		
Terpineol	84		84					
Polyethylene dodecyl glycol ether		48						

the contact angle is, therefore, a measure of the competing tendencies of the drop to spread. It is beneficial to know about the influence of the flotation agent on the wettability of plastics to set its optimal concentration. First, the contact angles were measured with both distilled and tap water. In both cases the average value was 84° and shows no difference in wettability when using distilled or tap water. When these data are compared with the published results $(90^{\circ} [5],$ 91° [6,7], 86° [2], 88° [8]), it is necessary to consider that most authors do not specify the exact plastic type. Standard (GP) and high-impact (HI) polystyrene differ in their properties, e.g., in density (990 and 1030 kg/m³) [9]. Also, different components are often added to plastics during industrial production, which may influence the properties of the plastics, such as wettability. This might explain the difference in the wettability of polystyrene. Polystyrene exists in a number of modifications with contact angles differing by up to 10° .

Contact angles measured at different concentrations of flotation agents are given in Table 3. The wetting agents, tannic acid and calcium lignosulfonate, decrease the contact angle by up to 7° and cause higher wettability of polystyrene. Very interesting is the behavior of polyethylene glycol dodecyl ether, which is extensively used as a detergent and a wetting and emulsifying agent. Polyethylene glycol dodecyl ether combines properties of frothers and wetting agents, strongly decreases the surface tension of the flotation liquid, forming a compact foam (frother), and, at the same time, increases the wettability of polystyrene. Already at a concentration of 20 mg/l the contact angle is 48° and the wettability increases additionally at higher concentrations.

Unfortunately, it was not possible to measure small contact angles using the method mentioned above.

3.3. Flotation

The flotation recovery was measured in tap water and in solutions of flotation agents. Here, the recovery is defined as a ratio of a component separated from the flotation vessel to the original amount of this component at the beginning of the experiment. The results are listed in Table 4. Fig. 1 demonstrates the concentration dependence of surface tension, contact angle, and flotation recovery for each flotation agent.

The plastics surfaces are made up of low-energy organic compounds and some polymers, including polystyrene, contain no polar groups. Different authors have suggested various mechanisms for the adsorption of reagents on plastics. Most popular is the model proposed by Fraunholz [2,10]: The adsorption of depressants on plastics is mainly driven by physisorption. The interaction forces include hydrophobic interactions and electrostatic forces. Further, zeta-potential measurements indicate nonselective adsorption of surfactants. The cations have a profound influence on the adsorption of polyelectrolytes, mainly because they reduce the repulsion between the charged segments, which facilitates adsorption. The adsorption mechanism can be considered on a microscopic scale as well [11]. The solid surface can be divided into very small segments, which represent homogeneous areas with respect to their wettability. The wettability is here determined by the polarity of the molecule groups that dominate the segment. Thus, the wettability of a micro-

Table 4
Flotation recovery of polystyrene in solutions of flotation agents and its concentration dependence

Flotation agent	Flotation recovery (%)							
	0 mg/1	20 mg/l	40 mg/l	60 mg/l	80 mg/l	100 mg/l		
Calcium lignosulfonate	98.1	12.2	5.2	7.7	4.4	5.8		
Tannic acid	98.1	79.4	29.7	18.9	10.9	2.0		
Terpineol	98.1	100	100	100	100	100		
Polyethylene dodecyl glycol ether	98.1	100	100	98.8	62.4	40.5		



Fig. 1. The concentration dependence of surface tension, wettability, and flotation recovery of polystyrene for the flotation agents terpineol, polyethylene glycol dodecyl ether, calcium lignosulfonate, and tannic acid.

scopic surface is determined by the ratio of hydrophilic to hydrophobic segments. A molecule of polystyrene does not incorporate any polar groups; it includes only a hydrophobic aromatic ring, connected to the carbon chain. From this point of view the adsorption mechanism should be simple, and both the wettability and the flotability depend in the first place on the concentration of the flotation agents.

The aim of this article is the study of the mutual relationship between the flotability and wettability of plastics (specifically polystyrene) at different concentrations of flotation agents. Frothers, supporting the foam production and stability, play a significant role during the flotation process. A frother terpineol belongs to the most simple and commonly used type of nonionic surfactants. The experiments confirmed that this reagent does not influence the wettability of polystyrene. Its aqueous solution has a surface tension lower than that of water; it foams easily and contributes to the high flotability of each plastic, including polystyrene. The influence of TEGD ether is more complicated. This compound contains a large, highly hydrophilic polar group and a long hydrocarbon chain and belongs to the group of nonionic surfactants. It is strongly surface-active and according to the literature [12] as well as our own experimental data it can be concluded that in the concentration range 20-30 mg/l the formation of micelles takes place. At lower concentrations (up to 20 mg/l) the surface tension decreases significantly (31.4 mN/m) and the frothing effect dominates. In contrast, at higher concentrations, the presence of this surfactant increases the wettability, which leads to decrease of the flotation recovery. According to visual observations the solution with a concentration of 60 mg/l wets the polystyrene surface practically completely. The strong depressant effect should be the outcome of the reduced liquid surface tension [2]. However, the flotability of polystyrene

decreases at markedly higher concentrations than wettability or surface tension do.

Macromolecular depressants are widely used to suppress flotation of naturally hydrophobic materials. However, the adsorption mechanism for these compounds is not fully evident. The present work has studied the behavior of two depressants-calcium lignosulfonate, which counts among polyelectrolytes, and tannic acid, a macromolecular nonionic depressant. The simplest model of wetting agent behavior assumes that contact angle decrease implies lower flotability. Comparing experimental data measured for calcium lignosulfonate and tannic acid, we found the presumption to be invalid. The flotability of tannic acid decreases linearly with increasing concentration and the recovery reaches only 2% at the concentration 100 mg/l. In contrast, the flotability of calcium lignosulfonate sharply decreases already at a concentration of 20 mg/l and, furthermore, at higher concentrations the recovery does not change (average 5%). From experimental data it can be deduced that there is a certain difference in the adsorption mechanisms of these two agents. Adsorption of both types of depressants occurs only if the repulsion between molecular segments is sufficiently attenuated by counterions [2]. Adsorption behavior of lignosulfonates (anionic polyelectrolytes) was studied in detail. It was found [13] that the action of lignosulfonate cations is dominant (Na⁺, NH_4^+ , Ca^{2+}) and the addition of bivalent cations, especially Ca^{2+} , amplifies the depression. The authors recommend the use of tap water because of its higher mineral content in comparison with distilled water. The Ca^{2+} ion, because of its two positive charges, is presumed to play the role of a bridge between the plastic surface and lignosulfonate. Tannic acid, which is a nonionic agent, contains two types of molecular groups capable of adsorbing on a surface-carboxyl and phenolic groups. It was found [14] that only one type of phenolic group is active. It is an undissociated radical containing an aromatic ring with three hydroxyl groups.

Analogous data on flotability of plastics as a function of the concentration of various depressants can be found in the literature. In the case of polyethylene terephthalate (PET) [10], tannic acid shows a distinct depressing effect (at a concentration of 0.1 g/l the flotability is about 20%, whereas for sodium lignosulfate, which is similar to calcium lignosulfonate, it is 60%). In contrast, in the case of polycarbonates (PC) [15], it is sodium lignosulfonate that has a noticeable depressing effect (at a concentration of 0.1 g/lthe flotability of PC is about 20%, whereas in the presence of tannic acid it reaches 90%). The comparison of the structure of these three polymers (PS, PET, and PC) leads to the assumption that macromolecular depressants of the polyelectrolyte type adsorb more quickly on such polymers, which do not contain oxygen molecules in their structures. The adsorption of the depressant is then enabled by the presence of ions such as Ca²⁺ and Na⁺. On the other hand, the nonionic macromolecular depressants (especially tannic

acid) are more easily bound by polymers containing oxygen molecules.

4. Conclusions

In this article the reciprocal relationship between the flotability and wettability of plastics (specifically polystyrene) was studied at different concentrations of flotation agents. Terpineol, as a representative of the simplest type of frothers, does not affect the plastic wettability, and its presence especially influences the properties of the flotation solution. The agent polyethylene glycol dodecyl ether, formally assigned to frothers due to high surface activity, enhances the wettability of polystyrene considerably and above a concentration of 60 mg/l decreases the flotability. The flotability of polystyrene, however, is lowered at markedly higher concentrations than the wettability or surface tension. This behavior will be the object of further studies.

The curves representing the dependence of polystyrene wettability on the concentrations of tannic acid and calcium lignosulfonate have similar shapes, whereas the curves describing the concentration dependence of flotability diverge completely. On one hand, the addition of calcium lignosulfonate already leads to a considerable decrease of the flotability at a low concentration of this agent; on the other hand, the flotability of polystyrene decreases almost linearly with increasing concentration of tannic acid. These conclusions demonstrate the difference in the adsorption mechanisms of the two agents. Macromolecular depressants of the polyelectrolyte type adsorb more quickly on such polymers, which do not contain oxygen molecules in their structures. The adsorption of the depressant is then enabled by the presence of ions such as Ca^{2+} and Na^+ . On the other hand, the nonionic macromolecular depressants (especially tannic acid) are more easily bound by polymers containing oxygen molecules.

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Collision processes involving a single rising bubble and a larger stationary spherical particle

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ABSTRACT

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Keywords: Flotation Multiphase flow Bubble-particle interaction Collision efficiency Bubble trajectory The adhesion of bubbles to a particle surface is a ubiquitous natural phenomenon that plays a critical role in numerous industrial processes. The aim of this work is to broaden the knowledge of the hydrodynamic interactions that occur between bubbles and solids of a comparable size. Focusing on collision processes between a single rising bubble with an immobile surface ($D_b < 1 \text{ mm}$) and a larger stationary solid spherical particle, the bubble trajectory, collision efficiency and maximum collision angle were determined experimentally. All existing theoretical models of mineral floatation are based on the fundamental assumption that liquid flow around the bubble is both fore-and-after asymmetric in a vertical orientation and left-andright symmetric in a horizontal orientation. However, when a small bubble collides with a larger spherical theoretical models enabling the estimation of the collision efficiency or maximum collision angle were tested for description of collision processes between bubbles and solids of a comparable size.

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1. Introduction

The formation of bubble-particle aggregates, caused by bubbleparticle interaction, is a fundamental process occurring in many industrial applications. Flotation is one of the most important examples of such a process. Originally developed in the mining industry to recover valuable minerals from mined ores, flotation employs air bubbles as carriers to recover hydrophobic entities from complex slurries. Due to its high separation efficiency, cost effectiveness and simplicity of operation and maintenance. flotation has been extended to other industries utilising solid-solid and solid-liquid separation processes. Such processes include: bitumen recovery from oil sands; the de-inking of recycled paper pulp; de-oiling in heavy oil exploration; the removal of fine solids in industrial and domestic water treatment; the treatment of multiphase toxic effluents in the chemical and mining industries; and, plastics separation and recycling. The use of flotation in plastics separation has grown in line with the need to recycle plastics (e.g. Shent et al., 1999; Dodbiba and Fujita, 2004). However, most previous studies have been based on the needs of mineral flotation, and, consequently, have focused on particles that were much smaller than the bubbles. There is a fundamental difference in the interaction between plastics particles and bubbles in plastic flotation. The size of the plastic particles is measured in millimetres and, thus, the floating

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aggregate is usually formed by one particle and a number of adhered bubbles. In mineral flotation the floating aggregate is usually formed by one bubble and a number of adhered particles. Our work contributes to a better understanding of the bubble–particle interaction process when the particle is larger than the bubble. A stationary spherical particle was chosen as a model particle imitating plastic material. We focussed only on the collision process between this stationary particle and one raising bubble; here bubble and particle sizes play the most important role in all calculations. A methodological description of such collision process is followed by experimental results, which are then compared with those obtained by theoretical models of mineral flotation.

2. Bubble-particle interaction theory

An identical mechanism of bubble–particle interaction can be assumed for both types of flotation (mineral flotation with $D_p/D_b < 1$; plastics flotation with $D_p/D_b > 1$; here D_p and D_b are the particle and bubble diameters, resp.). For efficient bubble–particle capture, a sufficiently close encounter is required. The process is initially controlled by the hydrodynamics governing bubble–particle approach in the liquid phase. As the particle and bubble come closer, the influence of intermolecular and interfacial forces increases. The liquid film between the bubble and particle surfaces begins to drain away, causing the film to rupture. The three-phase (air–water–particle) contact line becomes larger until a stable wetting perimeter is established, and, at this point, a stable bubble– particle aggregate is formed. This bubble–particle interaction process is usually described as consisting of a sequence of three discrete steps (Derjaguin and Dukhin, 1960; Nguyen et al., 1997; Ralston et al., 1999;

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Ralston et al., 2002; Nguyen and Schulze, 2004): (i) collision – approach of the bubble and the particle to the contact distance; (ii) attachment – adhesion of the particle to the bubble surface when the particle is smallerRESS than the bubble, or adhesion of the bubble to the particle surface when the bubble is smaller than the particle. The attachment process begins with the drainage and rupture of the liquid film, and continues with contact line movement; (iii) stability – detachment of the bubble from the particle surface occurs when the bubble–particle aggregate is unstable.

In mineral flotation, particle motion around a rising bubble is commonly considered as motion around a spherical body with rotational symmetry in the gravitational direction. To describe liquid flow around an air bubble it is convenient to choose an axisymmetrical (polar spherical) coordinate system and a three-dimensional (3D) analysis of bubble-particle interaction is often simplified into a twodimensional (2D) analysis. The liquid flow around bubbles typically used in flotation is fore-and-aft asymmetric (Nguyen, 1999), and strongly affects the encounter and attachment mechanisms. Due to the asymmetry of liquid flow, small particles can be pushed away from the bubble surface despite the fact that the distance of such particles from the bubble vertical axis is less than the bubble radius. The critical trajectory, known as the grazing trajectory, distinguishes the trajectories of particles that encounter the bubble from the trajectories of those that do not, and is characterized by the critical radius R_c and the critical collision angle $\varphi_{c max}$. Here, the polar angle φ is measured at the bubble centre and from the front stagnation bubble point. The typical scheme of bubble-particle interaction in mineral flotation is illustrated in Fig. 1A. Bubble-particle interaction in plastics flotation, in which the particle is larger than the bubble, is described in Fig. 1B. The bubble grazing trajectory (grazing radius R_c) restricts the collision area within which a bubble collides with a particle. Here, the polar angle φ is measured at the particle centre and from the particle vertical bottom half-axis.

2.1. Bubble motion in an aqueous solution of a surface-active agent

The hydrodynamic field around a moving bubble in stagnant liquid can be described using the Navier–Stokes equations (e.g. Nguyen, 1999), any solution of which must satisfy all boundary conditions at the bubble surface. A general analytical solution does not exist, but it is possible to solve these equations in two extreme cases: for small bubbles (Re <1, Stokes conditions); for large bubbles ($Re \gg 1$, potential conditions). The Reynolds number (Re) is defined as

$$Re = \rho_{\rm l} U_{\rm b} D_{\rm b} / \eta_{\rm l} \tag{1}$$

Here, ρ_l and η_l are the liquid density and dynamic viscosity; D_b and U_b are the bubble diameter and bubble rise velocity, respectively. At small Reynolds numbers, the bubble rise velocity is given by the Stokes equation:

$$U_{\rm b,Stokes} = \frac{2R_{\rm b}^2 g(\rho_{\rm l} - \rho_{\rm b})}{9\eta_{\rm l}}.$$
(2)

Here the bubble has an immobile surface and its velocity is the same as that of a solid sphere. The drag coefficient C_D is well correlated to the Reynolds number (Clift et al., 1978; Michaelides, 2006) by the function:

$$C_{\rm D} = 24 / Re.$$
 (3)

For bubbles with a diameter of more than 0.2 mm, the properties of the liquid medium play an important role. Since the mechanism was first described by Frumkin and Levich (1947) and Levich (1962), the impact of surfactants on velocity reduction has been well documented (Clift et al., 1978; Dukhin et al., 1998; Michaelides, 2006; Nguyen and Schulze, 2004). The motion of bubbles in a liquid is influenced by the kinetics of surfactant



Fig. 1. Scheme of bubble–particle interaction process. A – single rising bubble and small falling particle; B – small rising bubble and large stationary particle. Grazing trajectory with radius $R_{\rm c}$, maximum initial angle $\varphi_{0,\rm max}$ and maximum collision angle $\varphi_{\rm c,max}$ are denoted.

transport. The surfactant concentration varies along the surface of a bubble, reaching its maximum level at the rear stagnation point and its minimum level at the front stagnation point. During bubble rise in a surfactant solution, surface contamination often creates an immobile cap on the rear surface around the stagnation point, while the front part of the bubble surface remains mobile. When this happens the front part of the bubble becomes stretched, and the rear part becomes compressed. Due to the gradient of the surfactant concentration, a gradient exists along the bubble surface at the interface between the bubble and liquid. This gradient retards the surface of the bubble, and strongly affects the local stress balance at the bubble-liquid interface. Therefore, the drag on a bubble in a surfactant solution is less than that on a solid particle, but greater than that on a bubble in pure water. As the use of non-linear Navier-Stokes equations makes it very difficult to achieve an analytical solution in the case of intermediate Reynolds numbers, empirical models are often used to predict bubble rise velocity.

Nguyen and Schulze (2004) recommended two types of semiempirical equations, depending on the value of the Reynolds number. For small bubbles in contaminated water, the bubble shape is spherical and the drag coefficient corresponds to that of solid particles. The bubble terminal velocity $U_{\rm b}$ thus given is:

$$U_{\rm b} = U_{\rm b,Stokes} / \left\{ 1 + \frac{Ar / 96}{(1 + 0.079Ar)^{0.755}} \right\}.$$
 (4)

In this equation, $U_{\text{b,Stokes}}$ is the bubble velocity predicted by Stokes's law (Eq. (2)) and *Ar* is an Archimedes number defined as

$$Ar = \frac{g\rho_l(\rho_l - \rho_b)D_b^3}{\eta_l^2}.$$
(5)

Here, $\rho_{\rm b}$ is the air density and *g* is the coefficient of gravity acceleration. The drag coefficient $C_{\rm D}$ for a bubble in contaminated water starts to deviate from the standard curve at approximately Re = 130. When bubble shape is taken into account the drag coefficient $C_{\rm D}$ is found to be almost constant ($C_{\rm D} = 0.95$).

Karamanev and Nikolov (Karamanev and Nikolov, 1992; Karamanev, 1994) formulated a semi-analytical equation linking bubble rise velocity to bubble shape:

$$U_{\rm b} = \left(\frac{8g}{6^{2/3}\pi^{1/3}C_{\rm D}}\right)^{1/2} V_{\rm b}^{1/6} \cdot a_{\rm T} \cdot T a^{b_{\rm T}}.$$
 (6)

In this equation, V_b is the bubble volume and the drag coefficient C_D is calculated using the correlation of the drag coefficient for light particles where Re < 130:

$$C_{\rm D} = \frac{24(1+0.173Re^{0.657})}{Re} + \frac{0.413}{1+16300Re^{-1.09}}$$
(7)

where Re>130, $C_D = 0.95$. The Tadaki number (*Ta*) is relative to the Reynolds *Re* and Morton *Mo* numbers (Nguyen and Schulze, 2004):

$$Ta = Re(Mo)^{0.23},\tag{8}$$

$$Mo = \frac{g\eta_{\rm l}^4}{\rho_{\rm l}\sigma^3}.\tag{9}$$

The empirical constants a_T and b_T (Eq. (6)) are calculated with respect to bubble shape (Nguyen and Schulze, 2004): for a spherical bubble ($Ta \le 2$), $a_T = 1$ and $b_T = 0$; for an ellipsoidal bubble ($2 \le Ta \le 6$), $a_T = 1.14$ and $b_T = -0.176$. The liquid surface tension is denoted as σ .

2.2. Collision efficiency in mineral flotation and plastics flotation

To simulate and analyse the whole bubble–particle interaction process, the effectiveness of such a process should be evaluated. Assuming that collision and attachment are independent sub-processes (Derjaguin and Dukhin, 1960), it is possible to simplify the calculation of the effectiveness of the whole bubble–particle interaction process by calculating the efficiency of each individual step. Focusing only on the collision process in mineral flotation, the collision efficiency E_c was defined as the ratio of the actual number of particles participating in the collision process per unit time N_{cr} to the ideal number of particles N_{ci} (Wang et al., 2003; Nguyen and Schulze, 2004). This can be described mathematically as follows:

$$E_{\rm c} = \frac{N_{\rm cr}}{N_{\rm ci}} \tag{10}$$

Experimental collision efficiency is most frequently determined from the particle grazing trajectory (radius R_c , see Fig. 1A), which distinguishes the trajectories of particles that encounter the bubble from the trajectories of those that do not. Based on a simple geometric interpretation of the grazing trajectory, one can obtain the following simple relation for bubble-particle collision efficiency (Nguyen and Schulze, 2004):

$$E_{\rm c} = \left\{ \frac{R_{\rm c}}{R_{\rm p} + R_{\rm b}} \right\}^2 = \sin^2(\varphi_{\rm o,max}). \tag{11}$$

Here $\varphi_{0,max}$ is the initial angle corresponding to the grazing trajectory. Having determined the grazing trajectory, it is then a relatively simple matter to use this relation to calculate collision efficiency. Taking into account the geometrical interpretation of bubble–particle interaction for $D_p > D_b$, (illustrated in Fig. 1B), it is also possible to use Eq. (11) to calculate collision efficiency in plastics flotation.

2.3. Collision efficiency models used in mineral flotation

The estimation of collision efficiency has been the focus of many published theories. Recently, Dai et al. (2000) presented a critical review of various models used for the purposes of mineral flotation. Therefore, only a short review is given here. Sutherland (1948) developed the first collision model, deriving E_c from fluid stream function by assuming an inertialess particle, unretarded bubble surface and potential fluid flow regime. For conditions of mobile bubble surfaces, the Dukhin (GSE) model is considered to be one of the most comprehensive models (Dukhin et al., 1995; Dai et al., 2000).

In most collision models, attention has been focused on bubbles with an immobile surface. This retardation is caused by tap water impurities and surface-active agents added during industrial flotation processes. Schulze (1989) proposed that bubble-particle collision results from the combination of three different effects, interceptional, gravitational and inertial, and thus derived a simple relation for the collision angle of the grazing trajectory ($\varphi_{c,max}$):

$$\varphi_{c,max} = 78.1 - 7.37 \log Re \text{ for } 20 < Re < 400$$
 (12a)

$$\varphi_{c,max} = 85.5 - 12.49 \log Re \text{ for } 1 < Re < 20$$
 (12b)

$$\varphi_{c,max} = 85.0 - 2.50 \log Re \text{ for } 0.1 < Re < 1.$$
 (12c)

Nguyen (1994) employed numerical methods for E_c calculation. In the derivation the following assumptions were made. Firstly, that bubble–particle collision is controlled by long-range hydrodynamic and gravitational forces. Secondly, that the distance between the particle and the bubble is negligible in comparison with their sizes. Thirdly, that the bubble behaves as a rigid sphere and, thus, the bubble surface is completely immobile. Finally, that bubble motion is unaffected by particles. Collision efficiency could, therefore, be expressed as:

$$E_{\rm c} = \frac{2U_{\rm b}D}{9(U_{\rm b}+U_{\rm p})Y} \left(\frac{D_{\rm p}}{D_{\rm b}}\right)^2 \left[\sqrt{(X+C)^2 + 3Y^2} + 2(X+C)\right]^2, \quad (13)$$

where $U_{\rm b}$ and $U_{\rm p}$ denote the bubble rise velocity and particle settling velocity respectively; $U_{\rm b} + U_{\rm p}$ expressing the approaching (relative) velocity between a bubble and particles. The dimensionless parameters *X*, *Y*, *C* and *D* are dependent on the bubble Reynolds number and are given by:

$$X = \frac{3}{2} + \frac{9Re}{32 + 9.888Re^{0.694}}$$
(14a)

$$Y = \frac{3Re}{8 + 1.736Re^{0.518}}$$
(14b)

$$C = \frac{U_p}{U_b} \left(\frac{D_b}{D_p}\right)^2 \tag{14c}$$

$$D = \frac{\sqrt{(X+C)^2 + 3Y^2 - (X+C)}}{3Y}.$$
 (14d)

Thus, the maximum collision angle may be predicted by

$$\varphi_{c.max} = \arccos(D). \tag{15}$$

Recently, Sarrot et al. (2005) published a new model for the calculation of collision efficiency that takes into account the effect of bubble surface contamination. The "stagnant cap" model was used, with the resulting bubble surface contamination being characterized via the angle θ_{cap} . The surfactant-free bubble surface ($\theta < \theta_{cap}$) moves with the liquid (mobile surface) while the contaminated zone ($\theta > \theta_{cap}$) behaves as a "stagnant cap" (immobile surface). According to this model, $\theta_{cap} = 180^{\circ}$ for bubbles with a mobile surface and $\theta_{cap} = 0^{\circ}$ for bubbles with an immobile surface. The maximum collision angle may be then predicted by the dimensionless parameters *X* and *Y* which are determined by the bubble Reynolds number *Re* and the angle of contamination θ_{cap} .

$$\cos\varphi_{c,\max} = \frac{\sqrt{X^2 + 3Y^2} - X}{3Y} \tag{16}$$

$$X = k_1 \left[\frac{15 + 3 \left(\frac{Re}{k_3} \right)^{0.75}}{15 + \left(\frac{Re}{k_3} \right)^{0.75}} \right]^{k_2}$$
(17)

$$Y = \frac{0.095Re}{1 + 0.045Re^{4/3}}.$$
(18)

The parameters k_1 , k_2 and k_3 are given as:

$$k_{1} = 2 \frac{\sin^{3}(\theta_{cap}/2)}{1 + \sin^{6}(\theta_{cap}/2)}$$
(19a)

$$k_2 = 1 + \frac{8}{3(1 - \sin(\theta_{cap}/2))^{3/2}}$$
(19b)

$$k_3 = \frac{\pi}{3} \frac{1 - \cos(\theta_{cap})}{\theta_{cap}} + \frac{1 + \cos(\theta_{cap})}{2}.$$
 (19c)

All given models and equations were published for purposes of mineral flotation. Unfortunately, no data were found for bubble–particle interaction processes where $D_p > D_b$. Therefore, in the discussion part our experimental data and results are compared with assumptions resulting from general concepts (e.g. bubble behaviour in front of the inclined wall).

3. Experimental materials and methods

Distilled, de-ionised water with a pH value of 6.13 and conductivity of 1.6 μ S/cm was used at 25 °C for all measurements. For the flotation experiments an aqueous solution of the surface-active agent terpineol (Fluka Company) was used at a concentration of 187 mg/l (22 ppm). The surface tensions of the distilled water and terpineol solution were 71.6 mN/m and 63 mN/m, respectively. Spherical glass balls with diameters of 6.97 mm, 10.0 mm or 15.0 mm were used for all measurements. These particles were cleaned and degreased in an equimolar mixture of sulphuric acid and hydrogen peroxide (Piranha). No additional surface modification (e.g. silanization) was done, because the quality of particle surface does not influence the collision process.

A schematic of the experimental apparatus is presented in Fig. 2. The setup consisted of the following main parts: (i) a rectangular glass column ($8 \times 6 \times 20$ cm) with a capillary – capillaries with inner diameters of 10, 15 or 20 µm were used to create bubbles in the diameter range of 0.3–0.9 mm; (ii) an air supply system consisting of a compressor, air reservoir, reduction valve and precision Omega valve; and (iii) a high-speed camera for monitoring bubble motion and encounter. Exposure was realized using a SCHOTT KL 2500 LCD cold light source.

Measuring began at a point 50 mm above the bubble detachment point at the top of the capillary. Bubble motion was measured over the next 100 mm to determine the local and terminal velocity profiles. A Redlake Motion Pro high-speed video camera was used at a capture frequency of 500 pictures per second and resolution of 1280×1024



Fig. 2. Schematic of experimental apparatus.



Fig. 3. Bubble rise velocity in a solution of surface-active agent as a function of bubble diameter. Comparison of experimental and theoretical data.

pixels. NIS-elements software was used for image analysis. Bubble size, particle size, bubble velocity, and the positions of the bubble and particle centres (x, y positions) were all measured.

4. Results and discussion

4.1. Bubble velocity in stagnant liquid

In order to compare the experimental results with the literature data, a high-speed video camera was used to measure terminal bubble velocity in the aqueous solution of a surface-active agent. The subsequent images (time interval 0.002 s) were used to calculate local velocity from the positions of the bubble centre. The mean velocity was then calculated from at least 30 positions, the standard deviation never exceeding 2%. Both our experimental results and other recently published data (Malysa et al., 2005) show that local velocity values are constant at a distance of more than 5 cm from the orifice. Therefore, we assume that measured velocity is equal to terminal velocity. Fig. 3 shows that bubble rise velocity was linearly dependent on bubble size. As described above, bubble motion is influenced by the kinetics of surfactant transport, bubble rise velocity being lower in surfactant solution than in pure water. Due to the small bubble size no rectilinear or zigzag bubble motion was observed, which is in accordance with theoretical assumptions (Clift et al., 1978). Our experimental data for bubble rise velocity were compared with theoretical data calculated using various models. For data prediction we used Nguyen and Schulze's (2004) model, described by Eq. (4), and Karamanev and Nikolov's (Karamanev and Nikolov, 1992; Karamanev, 1994) model, Eqs. (6–9). The results are plotted in Fig. 3. The velocities calculated using these models were almost identical and close agreement between the experimental data and the predicted data was evident in all cases.

4.2. Bubble – particle collision process

Bubble–particle collision is assumed to occur in the section of the particle surface between the angles $\varphi = 0$ and $\varphi = \varphi_{c,max}$, where angle φ is measured from the vertical particle axis, and $\varphi_{c,max}$ is the maximum possible collision angle (the theoretical maximum being 90°). The initial angle φ_0 characterises the initial position of the bubble centre with respect to the vertical particle axis. The values of φ_0 could lie within the interval 0° and $\varphi_{0,max}$, whereas the angle $\varphi_{0,max}$ corresponds to the grazing trajectory (see Fig. 1B). The collision angle φ_c is greater than φ_0 due to the deviation in bubble trajectory.

During our experimental measurements bubble motion was captured at intervals of 0.002 s prior to and during interaction with the surface of a stationary spherical particle. Having obtained the bubble centre coordinates (x_i , y_i) for this period of time, we were able to calculate the bubble rise velocity U_b and bubble radius R_b . The initial angle φ_0 and collision angle φ_c were evaluated from the captured images. Fig. 4 provides an example of the data obtained for changes in the trajectory of a bubble ($D_b = 0.707 \text{ mm}$) approaching the surface of a particle ($D_p = 10 \text{ mm}$); bubble trajectories for several initial bubble centre positions being shown. Each point represents the bubble centre position captured at successive intervals of 2 ms. The last point in the sequence is the collision point. Although the theoretical maximum initial angle is 90° (which is the case when the distance between the bubble and particle centres equals $R_p + R_b$), the actual maximum initial angle is, in reality, much smaller, as Fig. 4 shows for the last two sequences ($\varphi_0 = 73.5^\circ$, $\varphi_0 = 80.8^\circ$). For such initial bubble positions no collision was observed.

While the bubble remains moving parallel to the particle vertical axis no deviation occurs. Deviation in the trajectory of a bubble occurs and increases as the distance between the bubble centre and the particle vertical axis grows; namely, as the initial angle φ_0 increases. In the case of small bubbles ($D_b < 1 \text{ mm}$) a very small stream field is expected, only influencing bubble motion immediately prior to interaction with a particle (Dai et al., 1998; Ralston et al., 2002). Fig. 5 illustrates this fact by plotting the dependence of the collision angle on the initial angle; data for all the various different bubble and particle sizes used being collated in this figure.



Fig. 4. Trajectory deviation of bubble centre from particle vertical axis ($D_p = 10.0$ mm) for several initial bubble centre positions ($D_b = 0.707$ mm). The legend characterises the initial position of each bubble by the value of its initial angle.



Fig. 5. Dependence of the collision angle on the value of the initial angle (bubble diameters: $D_b = 0.3-0.9$ mm).

The experimental data clearly shows the linear dependence of the collision angle on the initial angle, the proportion constant being 1.04. These results are in close correspondence with theoretical assump-

tions (Dai et al., 1998; Nguyen, 1999) assuming asymmetric liquid flow. The symmetry of liquid flow is stronger for bubbles with an immobile surface than for those with a mobile surface.



Fig. 6. Bubble trajectories for different initial bubble centre positions in relation to particle vertical axis ($D_p = 15 \text{ mm}$, $D_b = 0.82 \text{ mm}$) – detail shown in B. The time interval between two successive images was 0.002 s. The legend characterises the initial bubble position by the value of the initial angle.



Fig. 7. Example experimental image of bubble trajectory ($D_p = 15 \text{ mm}$, $D_b = 0.82 \text{ mm}$, $\varphi_0 = 65.3^\circ$).

4.3. Maximum collision angle

The value most often used to characterise flotation effectiveness is efficiency which can be described by collision and attachment efficiencies. In Eq. (11) the value of collision efficiency is given by the maximum initial angle, $\varphi_{0,\text{max}}$ leading to a successful encounter process. In our experimental results, no collision occurred for initial angles greater than 75°. For such initial angles, the bubble trajectory deviates significantly from the linear direction and, consequently, the distance between particle and bubble centres is greater than $R_{\rm b} + R_{\rm p}$ during bubble motion. For various initial bubble centre positions close to the grazing trajectory, Fig. 6 shows bubble trajectories in relation to the vertical axis of the particle. The first two initial positions (63.4° and 65.3°) guaranteed reliable bubble-particle collisions, whereas no collision took place for the last two initial bubble positions (70.4° and 71.3°). The actual grazing trajectory was close to an initial angle of 66.8°, the moment of collision being indicated by the arrow. To illustrate the bubble trajectory close to the grazing trajectory, Fig. 7 captures experimental data over a time span of 0.04 ms ($D_p = 15$ mm, $D_{\rm b} = 0.82 \, {\rm mm}, \, \varphi_0 = 65.3^{\circ}).$

The experimental data on maximum collision angles are shown in Fig. 8, which plots the dependence of maximum collision angle $\phi_{c,max}$ against bubble diameter D_b for two particle diameters. From these data, it is clear that $\phi_{c,max}$ decreases as the bubble diameter increases and the particle diameter becomes smaller.

The experimental results were compared with the data published for various theoretical models. It should be noted that with our experimental conditions (contaminated water), an immobile bubble surface was expected. For bubbles with an immobile surface $(\theta_{cap} = 0^{\circ})$, Nguyen's model (Eqs. 13–15) is recommended (Sarrot et al., 2005). According to this model, the dependence of $\phi_{c,max}$ on D_b has a downward curve, which accords with our experimental results, although the calculated values of $\varphi_{c,max}$ are lower than our experimental ones. Therefore, we also considered models for mobile bubble surfaces ($\phi_{cap} = 180^\circ$; Eqs. 16–18; parameters $k_1 = k_2 = k_3 = 1$) and partially mobile bubble surfaces ($0^{\circ} < \theta_{cap} < 180^{\circ}$, Eqs. 17–19a–c). Here, the dependence $\phi_{c,max}$ on D_b has an upward curve, which is in substantial disagreement with our experimental data. These results make it clear that none of the recommended models (Nguyen, 1994; Sarrot et al., 2005) are suitable for estimating the maximum collision angle in plastics flotation. Before explaining the reason for this, the reader's attention is drawn to experimental and calculated data for four bubble sizes presented in Table 1. Here are given bubble Reynolds number in stagnant liquid and Reynolds number in the moment of collision with solid surface; then experimental maximum initial angle and experimental maximum collision angle. Maximum collision angles were calculated by theoretical models for immobile, mobile and partly mobile bubble surface.

According to Nguyen's model (Nguyen, 1994) the particles in mineral flotation are so small and the bubbles so large that bubble motion is unaffected by the particles. In a later model (1999), Nguyen assumes fore-and-aft axisymmetric liquid flow around bubbles, and, due to small particle size and weight, considers neither liquid motion nor deviated streamlines around a settling particle. However, this assumption is not met when $D_p > D_b$ and the bubble size is larger than 0.1 mm. The fore-and-aft axisymmetric motion of bubbles around a spherical particle can only be assumed for very small bubbles $(D_{\rm b} < 0.01 \text{ mm}, Re < 1)$ where changes in liquid flow around the bubble are negligible. For larger bubbles $(D_b > 0.1 \text{ mm})$ we must consider liquid flow not only around the bubble, but also around the particle. Bubble behaviour prior to collision with a stationary spherical particle is similar to bubble behaviour prior to collision with an inclined plane. Thus it could be possible to describe the hydrodynamics of liquid flow around a bubble near an inclined plane by characterization of forces, primarily the lift force, acting on the bubble (Ishii and Zuber, 1979; Hibiki and Ishii, 2007), or by the theory of lubrication (Moraga et al., 2006; Podvin et al., 2008). In both cases, a reduction in bubble rise velocity is observed; this reduction being dependent on bubble size and inclination angle (Basařová et al., 2008). Table 1 shows the bubble



Fig. 8. Dependence of maximum collision angle on bubble size and particle size. Comparison of experimental and theoretical data.

Table 1

Selected data for collision angle calculation. Experimental data: particle diameter D_p ; bubble diameter D_b ; Reynolds number in stagnant liquid Re_b ; Reynolds number at moment of collision $Re_{b,coi}$; maximum initial angle $\varphi_{0,max}$; maximum collision angle $\varphi_{c,max}$. Calculated data: maximum collision angle $\varphi_{c,max}$ for 4 types of bubble surface mobility.

Dp	D _b	Reb	Re _{b,col}	$\varphi_{0,\max}$	$\varphi_{\rm c,max}$	$\varphi_{c,max}$	$\varphi_{c,max}$	$\varphi_{\rm c,max}$	$\varphi_{c,max}$
				Experimental	Experimental	$\theta_{\rm cap} = 0^\circ$	$\theta_{\rm cap} = 90^\circ$	$\theta_{\rm cap} = 112^{\circ}$	$\theta_{\rm cap} = 180^\circ$
[mm]	[mm]	[1]	[1]	[°]	[°]	[°]	[°]	[°]	[°]
10	0.35	13.1	12.4	73.7	83.2	70.9	71.0	75.9	81.4
10	0.53	32.4	30.5	62.4	76.5	66.8	71.2	76.8	82.4
10	0.74	64.8	62.1	63.2	72.7	64.4	72.2	78.7	83.9
10	0.97	110.6	98.1	55.7	59.7	62.9	73.2	80.3	85.0

Reynolds numbers in stagnant liquid (*Re*), calculated from experimental terminal bubble rise velocity, and the Reynolds numbers prior to collision (Re_{col}), calculated using the local bubble rise velocity. The decrease in the values of Re_{col} is significant. Therefore, although the utilization of barrier models for the description of bubble–particle interaction in plastics flotation is outside the scope of this article, it will be studied in a separate project.

4.4. Collision efficiency

The experimental collision efficiency was calculated using the maximum initial angle $\varphi_{0,lim}$, which describes the grazing bubble trajectory (Eq. (11)). Fig. 9 shows the dependence of collision efficiency on both bubble size and particle size. For the smaller bubbles $(D_{\rm b} < 0.7 \text{ mm})$, collision efficiency was roughly constant, although higher at larger particle sizes; the mean collision efficiency being $80 \pm 3\%$ for $D_{\rm p} = 10$ mm, and $88 \pm 3\%$ for $D_{\rm p} = 15$ mm. Collision efficiency decreased significantly for larger bubbles ($D_{\rm b}$ = 0.7–1 mm), which might be explained by a combination of higher bubble rise velocity, increasing bubble shape deformability, and the ratio of mobile to immobile bubble surface. However, comparing our experimental data with the results published for theoretical models can be misleading. All models of mineral flotation are based on the fundamental assumption that liquid flow around the bubble is fore-and-after asymmetric in a vertical orientation and left-and-right symmetric in a horizontal orientation. This hypothesis is justified for small particles that do not influence the steady motion of a bubble. However, when a small bubble approaches, or collides with, a larger spherical particle, liquid flow around the bubble is asymmetric from all points of view and, simultaneously, a change in the liquid flow around the bubble leads to a significant decrease in bubble velocity. Furthermore, the bubble surface mobility has a significant effect. Therefore, the development of a simple theoretical model for estimating collision efficiency in plastics flotation will be the focus of a later project.

5. Conclusion

We compared the bubble-particle interaction processes in mineral flotation and plastics flotation. This experimental study was focused only on the collision process between smaller rising bubble in contaminated water and larger stationary spherical particle which was chosen as a model particle imitating plastic material. In the case of small bubbles an insignificant liquid stream field was detected, only influencing bubble motion immediately prior to interaction with a particle. For an example, the linear dependence of the collision angle on the initial angle with low value of proportion constant was found. Although many features were confirmed to be common for both processes (mineral flotation and plastics flotation), significant differences also exist. In particular, plastics flotation shows that the flow of liquid around a bubble approaching, or colliding with, a larger stationary spherical particle is asymmetric. However, this has not been taken into account by models of mineral flotation, which means that they cannot be used to reliably estimate collision efficiency as well as maximum collision angle.

Notation

- Ar Archimedes number
- C_D drag coefficient
- D diameter, m
- *E*_c collision efficiency
- g gravity acceleration, m s⁻²
- Mo Morton number
- R radius, m



Fig. 9. Dependence of collision efficiency on bubble size and particle size.

Re	Reynolds number
Та	Tadaki number

U

velocity, ms⁻¹ V

volume. m³

Subscripts

Subscrip	115
b	bubble
~	collicion

L	COMISION
1	liquid

liquid

- max maximum
- particle р rel relative

Greek letters

dynamic viscosity, kg m⁻¹ s⁻¹ n

- collision angle φ_{c}
- φ_0 initial angle
- density, $kg m^{-3}$ ρ
- surface tension, mN m^{-1} σ
- θ free bubble surface

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Collision of a small rising bubble with a large falling particle

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ABSTRACT

The attachment of bubbles onto a collecting surface plays a critical role in flotation which is utilised for the separation of mineral ores, coal or plastic materials. While mineral flotation deals with fine particles and larger bubbles, this work is focused on the opposite case of an interaction of a single rising bubble ($D_b < 1 \text{ mm}$) with a larger spherical particle, which falls down through a stagnant liquid. The collision is studied theoretically and experimentally. The theoretical model, based on an analysis of forces acting on the bubble, leads to a differential equation for the bubble motion. Both the mobile and immobile bubble surfaces are considered. The experimental bubble trajectory and velocity evolution are in good agreement with the theoretical model. The horizontal deflection of the bubble trajectory caused by the particle motion is dependent on the ratio of bubble terminal velocity and particle settling velocity. The influence of buoyancy, interception and inertial mechanisms on the collision efficiency is also examined. It is concluded that the buoyancy is the most significant mechanism for the interaction of small bubbles with large particles.

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1. Introduction

The gas-liquid-solid three-phase systems are found in many industrial applications. An important one is the separation of solid materials by flotation. This process is based on the ability of some solids to remain attached to the gas-liquid interface. Particles of such a solid then agglomerate with bubbles and are floated to the liquid surface, from which they can be easily separated. The flotation was originally used for the separation of coal or mineral particles from the mined ore deposits. Owing to its simplicity and high efficiency, the flotation is nowadays also used for separation of oil sands, print inks in paperrecycling, waste water treatment and also for the separation of various plastic materials in their recycling process. In the standard flotation process, the particles are usually much smaller than the bubbles (we refer to these size proportions briefly as mineral flotation thereinafter). Oppositely in the case of plastics flotation, the particles are of comparable or even bigger size than bubbles. The inverted size proportion changes the mechanics of bubble-particle interaction (Alter, 2005). To develop a suitable model for predicting the efficiency of the plastics flotation, it is required to get the detailed description of the bubbleparticle interaction, i.e. of their approach, attachment and eventual detachment (Nguyen and Schulze, 2004). The theoretical models for predicting the flotation efficiency (e.g. Dai et al., 2000; Nguyen and

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Schulze, 2004) were developed for the mineral flotation. Due to modified mechanics, these models cannot be used for the plastics flotation with the inverted size proportions.

The first theoretical description of collision of a small particle with a large bubble was provided by Sutherland (1948). His model is based on the fact that the liquid streamlines are denser near the equator of the rising bubble. Particles move along the streamlines and some of them approach the bubble to a distance, which is smaller than the particle radius, and thus collide with the bubble surface. Sutherland assumed potential flow around a spherical bubble, and particles. which perfectly follow the liquid motion, and obtained an expression for the collision efficiency. Many conceptually similar models were developed later. Their reviews are available (e.g., Dai et al., 2000). For example, Flint and Howarth (1971) considered motion of the particle relative to the moving liquid due to particle settling. The model of Yoon and Luttrell (1989) covers all the flow regimes (Stokes, intermediate and potential) around the bubble. Other models consider a relative motion of the particle and liquid due to inertial and gravity forces (e.g., Schulze, 1989). The GSE model (Dai et al., 1998, 1999; Ralston et al., 1999) considers the particle inertia as well as (im)mobility of the bubble surface, and solves the particle motion via Basset-Boussinesq-Oseen equation. Recently, Huang et al. (2012) studied the particle motion using the rigorous equation for particle motion (including lift and Basset forces acting on the particle) and a fully resolved flow around the bubble.

The above mentioned models were developed for interactions of small particles with large bubbles and they are not suitable for the case of plastics flotation with inverted size proportions. Some studies of the small bubble–large particle interactions were published

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(e.g. Singh, 1998; Drelich et al., 1999; Shen et al., 2002; Pascoe and O'Connell, 2003; Basařová et al., 2010); however, these works provide mostly experimental results on the flotation yield as a function of various parameters, but not a fundamental study of the interaction mechanics.

The aim of this work is to broaden the knowledge of hydrodynamic interactions that occur between bubbles and solids of a comparable size or between larger particle and smaller bubble. Focusing on collision processes between a single rising bubble ($D_b < 1 \text{ mm}$) and a larger falling solid particle in stagnant liquid, a model describing the bubble trajectory is given here. The model assumes potential flow around the particle and balances forces acting on the bubble, leading to a differential equation for its motion. The bubble is considered spherical and can be either clean (with mobile interface) or contaminated (immobile interface). The particle is also spherical and moves vertically downward with a steady velocity. The model is validated experimentally by comparing observed trajectories with the computed one. The collision efficiencies are evaluated. At the end, it is found that the resulting efficiencies are governed mostly by the buoyancy and interception mechanisms and the inertial effects are only minor. For this situation, a simple expression for the collision efficiency is derived.

2. Model for the bubble motion

2.1. System of reference

The coordinate system is introduced as shown in Fig. 1. The frame of reference, either Cartesian (x, z) or spherical (r, θ), moves together



Fig. 1. System of reference frame and symbols.

with the particle, and its origin is fixed in the particle's centre. The particle radius is denoted R_p and the velocity of particle fall is U_p . The liquid has density ρ and viscosity η . The density of gas inside the bubble is ρ_p .

In the frame of reference, which moves together with the particle, the liquid is observed to move upward with the velocity U_p at locations far away from the particle. In the vicinity of the particle, the liquid velocity is characterized by velocity vector **u** (with components u_r and u_{θ}). The bubble (with radius R_b , diameter D_b and volume V_b) is located at position characterized by spherical coordinates r_b and θ_b . The bubble velocity vector is denoted as **u**_b (with components u_{br} and $u_{b\theta}$) and its acceleration **a**_b. Both vectors can be expressed in spherical coordinates

$$\begin{aligned} u_{br} &= \frac{dr_b}{dt} & u_{b\theta} = r_b \frac{d\theta_b}{dt} \\ a_{br} &= \frac{d^2 r_b}{dt^2} - r_b \left(\frac{d\theta_b}{dt}\right)^2 & a_{b\theta} = r_b \cdot \frac{d^2 \theta_b}{dt^2} + 2 \frac{dr_b}{dt} \frac{d\theta_b}{dt} \,. \end{aligned} \tag{1}$$

Here, *t* is time. The second term in the expressions for radial and tangential components of the acceleration is the centripetal and Coriolis acceleration, respectively.

2.2. Potential flow and pressure field around a sphere moving through a stagnant liquid

The liquid flow in front of the moving particle can be approximated by potential flow, assuming it moves at high Reynolds number ($Re_p = \rho U_p D_p / \eta \gg 1$). The potential flow does not approximate the flow correctly in the boundary layer (whose thickness δ scales as $\delta/D_p \approx Re_p^{1/2}$), and also in the upper hemisphere of the particle (the boundary layer separates close to $\theta \approx 95^{\circ}$).

The stream function for the potential flow around a sphere is (see e.g. Milne-Thomson (1996))

$$\psi = \frac{1}{2} U_p \left(1 - \frac{R_p^3}{r^3} \right) r^2 \sin^2 \theta = \frac{1}{2} U_p \left(1 - \frac{R_p^3}{r^3} \right) x^2.$$
(2)

The components of the liquid velocity

$$u_{r} = \frac{1}{r^{2} \sin \theta} \frac{\partial \psi}{\partial \theta} = \left(1 - \frac{R_{p}^{3}}{r^{3}}\right) \cos \theta \cdot U_{p}$$

$$u_{\theta} = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = -\left(1 + \frac{R_{p}^{3}}{2r^{3}}\right) \sin \theta \cdot U_{p}$$
(3)

The pressure *p* is determined by means of Bernoulli's equation,

$$p + \frac{1}{2}\rho\left(u_r^2 + u_\theta^2\right) = p_0. \tag{4}$$

The hydrostatic pressure $-\rho gz$ (where *g* is the gravity acceleration) is not included in the expression for the pressure. The reference pressure p_0 is adjusted in the way that *p* is zero far from the particle $(p_0 = \rho U_p^2/2)$, and one gets for the pressure field

$$p = \frac{1}{2}\rho U_p^2 \left(1 - \left(1 - \frac{R_p^3}{r^3} \right)^2 \cos^2\theta - \left(-1 - \frac{R_p^3}{2r^3} \right)^2 \sin^2\theta \right).$$
(5)

2.3. Forces acting on the bubble

The bubble motion is analysed via balance of forces, which acts on the bubble (see, e.g., Magnaudet and Eames (2000), or Thomas et al. (1983)). The momentum balance of a spherical bubble is written in the form

$$\rho_g V_b \mathbf{a}_b = \mathbf{F}_b + \mathbf{F}_d + \mathbf{F}_{hist} + \mathbf{F}_{am} + \mathbf{F}_I + \mathbf{F}_L + \mathbf{F}_{Lw}.$$
 (6)

The terms on the right-hand side are force contributions of different physical phenomena; these contributions are the buoyancy (\mathbf{F}_{b}), drag (\mathbf{F}_{d}), history force (\mathbf{F}_{hist}), added-mass force (\mathbf{F}_{am}), inertial force (\mathbf{F}_{l}), lift due to the vorticity (\mathbf{F}_{Lw}) and lift due to the flow restriction by the particle (\mathbf{F}_{L}). They will be discussed more in detail in following paragraphs and suitable expressions will be provided. The force contributions \mathbf{F}_{Lw} and \mathbf{F}_{hist} will be neglected. The term on the left-hand side represents the inertia of gas contained in the bubble, and it is negligible compared to the individual forces. The overall balance hence is

$$\rho_g V_b \mathbf{a}_b = \mathbf{F}_b + \mathbf{F}_d + \mathbf{F}_{am} + \mathbf{F}_I + \mathbf{F}_L \approx \mathbf{0}. \tag{7}$$

2.3.1. Buoyancy force

The radial and tangential components of the buoyancy force F_b are

$$F_{b,r} = (\rho - \rho_g) g V_b \cos \theta,$$

$$F_{b,\theta} = -(\rho - \rho_g) g V_b \sin \theta.$$
(8)

These expressions are valid if the bubble boundary is closed. It is not valid e.g. in such case, when a bubble is attached to a surface submerged in the liquid, because part of the bubble is not exposed to hydrostatic pressure.

2.3.2. Drag force

The drag force $\mathbf{F}_{\mathbf{d}}$ represents viscosity effects under condition of steady motion. This force is commonly expressed using a drag coefficient C_d as

$$\mathbf{F}_{\rm d} = -C_d \frac{\pi \cdot D_b^2 \cdot \rho}{8} (\mathbf{u}_{\rm b} - \mathbf{u}) |u_b - u|. \tag{9}$$

The vector $\mathbf{u}_{b} - \mathbf{u}$ is the relative velocity between the bubble and the liquid, and thereinafter, it is denoted as \mathbf{u}_{rel} . The drag coefficient C_d is a function of the bubble Reynolds number Re_b , which is

$$Re_{b} = \frac{\rho D_{b} |\mathbf{u}_{rel}|}{\eta} = \frac{\rho D_{b}}{\eta} \sqrt{\left(u_{b,r} - u_{r}\right)^{2} + \left(u_{b,\theta} - u_{\theta}\right)^{2}}.$$
(10)

The drag depends also on the presence of surface active contaminants in the system. For "clean bubbles" (no contaminants in the liquid), liquid exerts no shear on the bubble surface, and the gas–liquid interface is mobile (liquids move along bubble surface). The expression of Mei is appropriate for C_d (Mei and Adrian, 1992; Mei, 1994)

$$C_d = \frac{16}{Re_b} \left(1 + \left(\frac{8}{Re_b} + \frac{1}{2} \left(1 + 3.315 Re_b^{-1/2} \right) \right)^{-1} \right).$$
(11)

If surface active contaminants are present in the liquid, they adsorb at the interface and accumulate in the rear part of such a "contaminated bubble". The interface remains almost surfactant-free close to the front stagnation point, however, and the resulting gradients of surface tension are balanced by shear stress exerted by the liquid on bubble surface. In contrast to clean bubbles, this shear stress is non-zero and the bubble drag is therefore increased. The gas–liquid interface is immobilized to some extent (liquid motion is decelerated close to bubble surface). The flow around such a bubble and also its drag are well approximated by the behaviour of a solid particle with no-slip boundary condition for the liquid flow (e.g., Magnaudet and Eames, 2000). Schiller and Nauman (1935) suggested for the drag of solid spherical particles

$$C_d = \frac{24}{Re_b} \left(1 + 0.15Re_b^{0.687} \right) \tag{12}$$

and this dependence is applicable also for bubbles with surface immobilized by surfactants. Similar relation (Karamanev and Nikolov, 1992; Karamanev, 1994) was suggested for bubbles with fully immobile surface,

$$C_d = \frac{24}{Re_b} \left(1 + 0.173 Re_b^{0.657} \right) + \frac{0.413}{1 + 16300 Re_b^{-1.09}} \text{ for } Re_b < 130$$
(13)

and $C_d = 0.95$ for $Re_b > 130$.

The drag force described in Eq. (9) is valid only for a bubble in a uniform flow far from other boundaries. For the drag force near a wall, Kok (1993) received a correction by solving potential flow around a pair of bubbles (see de Vries et al. (2002) for more convenient form). When applying this correction, one receives for the component normal and parallel to the particle surface,

$$F_{d,r} = -C_d \frac{\pi \cdot D_b^2 \cdot \rho}{8} \left(u_{b,r} - u_r \right) \cdot \mathbf{u}_{rel} \cdot \left(1 + \frac{1}{4} \left(\frac{R_b}{r_b - R} \right)^3 \right)$$

$$F_{d,\theta} = -C_d \frac{\pi \cdot D_b^2 \cdot \rho}{8} \left(u_{b,\theta} - u_\theta \right) \cdot \mathbf{u}_{rel} \cdot \left(1 + \frac{1}{8} \left(\frac{R_b}{r_b - R} \right)^3 \right)$$
(14)

respectively.

2.3.3. The added-mass force

A bubble accelerating relative to the surrounding liquid has to overcome liquid inertia. The corresponding force, called added-mass force F_{am} , is (Magnaudet and Eames, 2000)

$$\mathbf{F}_{\rm am} = \rho V_b C_M \left(\frac{D \mathbf{u}}{D t} - \frac{d \mathbf{u}_b}{d t} \right) + \rho V_b (\mathbf{u} - \mathbf{u}_b) \frac{d}{d t} C_M, \tag{15}$$

where C_M is the added-mass coefficient, and its value is $C_M = 0.5$ in the case of a sphere in an unbounded fluid. Because we consider a potential flow (Eqs. (2) and (3)), the fluid acceleration at the position of the bubble can be expressed in terms of pressure gradient,

$$\frac{D\mathbf{u}}{Dt} = \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{1}{\rho} \nabla p.$$
(16)

A difficulty arises from the fact that C_M is different for the bubble motion in direction perpendicular or parallel to the particle's surface. This surface is approximated here as a flat wall. For the perpendicular and parallel motion, the added-mass coefficient is approximated by (Milne-Thomson, 1996)

$$C_{M,r} = \frac{1}{2} \left(1 + \frac{3}{8} \left(\frac{R_b}{r_b - R_p} \right)^3 \right),$$

$$C_{M,\theta} = \frac{1}{2} \left(1 + \frac{3}{16} \left(\frac{R_b}{r_b - R_p} \right)^3 \right),$$
(17)

respectively. The temporal variations of the added-mass coefficients therefore are

$$\frac{dC_{M,r}}{dt} = \frac{\partial C_{M,r}}{\partial r_b} \frac{dr_b}{dt} = -\frac{9}{16} \frac{R_b^3}{\left(r_b - R_p\right)^4} u_{br},$$

$$\frac{dC_{M,\theta}}{dt} = \frac{\partial C_{M,\theta}}{\partial r_b} \frac{dr_b}{dt} = -\frac{9}{32} \frac{R_b^3}{\left(r_b - R_p\right)^4} u_{br}.$$
(18)

The radial and tangential components of the added-mass force are obtained by writing (15) separately for these two directions, performing the derivative and by the use of (16) and (18), leading to

$$F_{am,r} = -C_{M,r} \cdot V_b \frac{\partial p}{\partial r} - C_{M,r} \cdot V_b \cdot a_{b,r} - \frac{9}{16} \frac{\rho V_b R_b^3}{\left(r_b - R_p\right)^4} (u_r - u_{br}) u_{br}$$

$$F_{am,\theta} = -C_{M,\theta} \cdot V_b \frac{1}{r_b} \frac{\partial p}{\partial \theta} - C_{M,\theta} \cdot V_b \cdot a_{b\theta} - \frac{9}{32} \frac{\rho V_b R_b^3}{\left(r_b - R_p\right)^4} (u_\theta - u_{b\theta}) u_{br}$$
(19)

If the liquid is still and the bubble moves perpendicularly to a large particle or wall, the added-mass force recovers the form presented by Legendre et al. (2005). The three terms on the right-hand side of Eq. (19) have their physical meaning: the first one is denoted as F_{aml} and it represents the added-mass force due to the liquid acceleration. The second term, denoted as F_{amb} , represents the added-mass force due to bubble acceleration. Finally, the last term, F_{amp} , is the added-mass force due to a change of relative position between the bubble and particle.

2.3.4. Inertial force due to liquid acceleration

Fluid acceleration around the particle leads to pressure gradients in the liquid, which causes a supplementary force F_I acting on the bubble, denoted as inertial force. Its radial and tangential components are

$$F_{I,r} = -V_b \frac{\partial p}{\partial r},$$

$$F_{I,\theta} = -V_b \frac{1}{r} \frac{\partial p}{\partial r}.$$
(20)

2.3.5. Lift force

When the bubble is close to the particle surface, the liquid motion around the bubble is restricted by the particle, and it squeezes in the gap between them. The liquid accelerates in this zone and the pressure decreases correspondingly, causing a lift force \mathbf{F}_L that pushes the bubble toward the particle surface. If the particle surface is approximated by a flat wall, a suitable expression for the lift force is found by de Vries et al. (2002). For the component perpendicular and parallel to the wall, it is

$$F_{L,r} = \frac{1}{2} \rho V_b \left(u_{\theta} - u_{b,\theta} \right)^2 \frac{\partial C_{M,\theta}}{\partial r_b},$$

$$F_{L,\theta} = 0.$$
(21)

For bubbles moving in a liquid, a supplementary lift force \mathbf{F}_{Lw} appears if the vorticity is present in the flow. The model presented here considers irrotational flow around the particle and such a lift is hence zero.

2.3.6. The history force

In the case of unsteady bubble motion, the effective force due to viscosity differs from the steady drag, expressed by (9). A supplementary viscous force due to unsteadiness, the history force \mathbf{F}_{hist} , is introduced (Magnaudet and Eames, 2000)

$$\mathbf{F}_{\text{hist}}(t) = -3\pi\eta D_b \int_{-\infty}^{t} K(t-\tau) \frac{\partial}{\partial \tau} (\mathbf{u}_{\text{b}}(\tau) - \mathbf{u}(\tau)) d\tau.$$
(22)

The kernel $K(t - \tau)$ is a function expressing the importance of the past accelerations on the actual viscous force. The Yang and Leal's (1991) kernel is suitable for the case of bubbles with mobile interface

$$K(t-\tau) = \frac{4}{3} \exp\left(\frac{36\eta(t-\tau)}{\rho D_b^2}\right) \operatorname{erfc}\left(\sqrt{\frac{36\eta(t-\tau)}{\rho D_b^2}}\right).$$
(23)

For the case of bubbles with immobile interface, the kernel by Mei and Adrian (1992) can be used,

$$K(t-\tau) = \left(\left(\frac{D_b}{2} \sqrt{\frac{\rho}{\pi \eta(t-\tau)}} \right)^{-1/4} + \left(\frac{D_b \eta f_h^3 (Re_b/2)}{\pi \rho |\mathbf{u}(t) - \mathbf{u}_b(t)|^3 (t-\tau)^2} \right)^{-1/2} \right)^{-2}.$$
(24)

Anyway, the history force is neglected in the present model. This is justified for the case of bubbles with mobile interface, but it is unfounded in the case of immobile interface. A practical reason for neglecting \mathbf{F}_{hist} is that equations of motion in form of ordinary differential equations are obtained, while preserving \mathbf{F}_{hist} leads to more complicated integro-differential equations.

2.4. Equation of motion for the bubble

The bubble motion is calculated by solving Eq. (7), to which the expressions for the forces are substituted. The added-mass force due to bubble acceleration F_{amb} , which contains the highest derivates of r_b and θ_b , is put to the left hand side of Eq. (7). After the substitution, we obtain for the radial and tangential components, respectively,

$$V_b \cdot \left(C_{M,r}\rho + \rho_g\right) \cdot a_{b,r} = F_{b,r} + F_{d,r} + F_{aml,r} + F_{amp,r} + F_{I,r} + F_{L,r} V_b \cdot \left(C_{M,\theta}\rho + \rho_g\right) \cdot a_{b,\theta} = F_{b,\theta} + F_{d,\theta} + F_{aml,\theta} + F_{amp,\theta} + F_{I,\theta} + F_{L,\theta}$$
(25)

By reducing the differential order of this equation, we get a system of equations

$$\frac{d}{dt} \begin{pmatrix} r_b \\ \frac{dr_b}{dt} \\ \frac{d\theta_b}{dt} \end{pmatrix} = \begin{pmatrix} \frac{dr_b}{dt} \\ \frac{d\theta_b}{dt} \\ r_b \left(\frac{d\theta_b}{d\tau} \right)^2 + \frac{F_{b,r} + F_{d,r} + F_{aml,r} + F_{amp,r} + F_{l,r} + F_{L,r}}{V_b \left(C_{M,r}\rho + \rho_g \right)} \\ - \frac{2}{r_b} \left(\frac{dr_b}{d\tau} \right) \left(\frac{d\theta_b}{d\tau} \right) + \frac{F_{b,\theta} + F_{d,\theta} + F_{aml,\theta} + F_{amp,\theta} + F_{l,\theta} + F_{L,\theta}}{V_b \left(C_{M,\theta}\rho + \rho_g \right)} \end{pmatrix}.$$

$$(26)$$

This system is solved numerically using subroutine ODE45 of MATLAB computational system. The initial condition (bubble position and velocity) is taken from the experimental data.

3. Experiments

3.1. Materials and apparatus

Pure water (distilled, de-ionised and de-mineralised water) was used at 25 °C for the measurements. The pH value was 6.13 and conductivity 1.6 μ S/cm. In addition, an aqueous solution of the surface-active agent terpineol (Fluka Company) was also used at a concentration of 187 mg/l (this solution is referred as contaminated water thereinafter). The surface tension (measured by du Nouy's ring method) was 71.6 mN/m and 63 mN/m for the pure and contaminated water, respectively. The particle was a smooth spherical glass ball with a diameter of 14.11 mm. It was cleaned and degreased in an equimolar mixture of sulphuric acid and hydrogen peroxide. No additional surface treatment was done, because the quality of particle surface does not influence the collision process.

The experimental measurements were done in a glass cell (50 cm height, 8 cm width and 6 cm depth). The scheme of experimental apparatus is given in Fig. 2. Single bubbles were created using a bubble generator built according to Vejražka et al. (2008). The bubble diameter ranged from 0.5 to 0.8 mm. The particle and light source were fixed to a translating unit, by which the particle motion was imposed with



Fig. 2. Scheme of experimental setup.

downward velocity of either 50 mm/s⁻¹ or 100 mm/s⁻¹. The bubble– particle interaction was observed by a high-speed camera Redlake Motion Pro, which was fixed to another translating unit. The camera moved together with the particle, so the bubble motion was recorded in a frame of reference moving together with the particle. The camera rate was 500 frames per second, image size was 1280 × 1024 pixels and the average image resolution was 14 µm/pixel. The images were analysed using NIS-Elements software, by which the bubble radius R_b , bubble position (x_i , z_i) and bubble velocity \mathbf{u}_b were determined.

Before experiments, particle position was carefully adjusted in respect to the bubble generator in the way that the other horizontal coordinate of the bubble is zero, y = 0.

3.2. Experimental conditions

Altogether, 16 sets of experimental data were obtained. These sets differ in the particle velocity (50 and 100 mm/s), bubble surface mobility (pure and contaminated water) and in bubble size ($D_b \sim 0.5$ mm, 0.6 mm, 0.7 mm and 0.8 mm; exact average diameters are given in figures reporting the results). For one experimental set, trajectories for at least ten initial positions x_0 were measured. Within one set of data, the variation of bubble size was about 1% and the maximum deviation from the mean did not exceed 3%.

In Fig. 3, the experimental terminal velocity of bubble rise U_b (measured for both pure and contaminated liquids) is shown. It is compared



Fig. 3. Experimental bubble rise velocity. Comparison with theoretical values.

with the prediction of Mei (1994), which is valid for mobile interface, and with correlation of Karamenev's relation (Karamanev and Nikolov, 1992; Karamanev, 1994) for immobile interface. The velocity calculated using these models is in close agreement with the experimental data, suggesting that the interface is either fully mobile or immobile in the pure and contaminated water, respectively. Owing to the small bubble size, no spiralling or zigzag bubble motion is observed during their rise. In Table 1, the bubble Reynolds number ($Re_b = \rho_l U_b D_b / \eta$), Weber number ($We_b = \rho_l U_b^2 D_b / \sigma$), Bond (Eötvös) number ($Bo_b = (\rho_l - \rho_g)gD_b^2 / \sigma$) and Stokes number ($St_b = (2\rho_l U_b R_b^2) / (9\eta R$)) are listed.

4. Results

4.1. Bubble trajectory

As a typical example, Fig. 4 shows data obtained within one experimental set. These data are provided for pure water, bubble diameter of 0.5962 mm and particle settling velocity of 50 mm/s. Several trajectories differing in the initial horizontal position of the bubble (x_0 , see legend) are shown. The grey lines illustrate the trajectory computed using the model with corresponding initial conditions. The positions of bubble centre in consecutive movie frames are denoted by symbols. The uppermost point shows the bubble position when it collides with the particle, with the exception of the outermost trajectory. The bubble with initial horizontal position $x_0 = 7.41$ mm does not collide with the particle. The bubble with initial position $x_0 = 6.68$ mm collides with the particle in its upper hemisphere. This collision is not predicted correctly by the model, because in the upper hemisphere, the real flow differs from the potential flow assumed in the model.

Fig. 5 shows an example of experimental results on the bubble velocity. Data originates from the same experiment as in Fig. 4. The relative velocity defined as the ratio between the bubble velocity at given time and bubble terminal velocity is plotted against the time to the collision. Despite the noise on experimental velocities, which originates in the differentiation and reaches about 5% of the measured value, the measured velocities (points) are in acceptable agreement with the model prediction (lines).

For bubble initial position close to the vertical particle axes, the velocity decreases monotonically. For more distant initial bubble position, the bubble velocity oppositely increases as a consequence of flow acceleration close to the particle equator. The flow near the rear part of particle cannot be modelled by the potential flow because the boundary layer detaches close to the equator and liquid recirculation appears behind this point. For the outermost position ($x_0 = 6.68$ mm in Fig. 7), we also observe that the experimental bubble velocity becomes lower than the prediction. We attribute this deviation to the influence of the separated flow (with much lower velocity) on the bubble.

l'able 1									
Theoretical	terminal	bubble	velocity,	bubble	Reynolds,	Weber,	Bond	and	Stokes'
numbers.									

D _b (mm)	U _b (m/s)	Re _b	We _b	Bob	St_b $U_p = 50$ mm/s	St_b $U_p = 100 \text{ mm/s}$		
Mobile bubble surface								
0.5	0.105	58.9	0.077	0.034	0.110	0.221		
0.6	0.142	95.1	0.167	0.049	0.159	0.318		
0.7	0.184	143.8	0.328	0.067	0.216	0.432		
0.8	0.231	207.2	0.596	0.087	0.282	0.565		
Immobile bubble surface								
0.5	0.057	31.8	0.026	0.039	0.110	0.221		
0.6	0.069	46.6	0.046	0.056	0.159	0.318		
0.7	0.082	63.9	0.074	0.076	0.216	0.432		
0.8	0.093	83.6	0.110	0.099	0.282	0.565		



Fig. 4. Example of experimental dataset on bubble trajectories. The particle diameter 14.11 mm, particle velocity 50 mm/s, bubble diameter 0.5962 mm, bubble terminal velocity 137.6 mm/s, and pure water.

4.2. Position of the collision

Most of the trajectories shown in Fig. 4 finish when the bubble comes into contact with the particle. This collision is characterized by its horizontal position x_{col} . The experimental dependence of x_{col} on the initial position x_0 is shown in Figs. 6 and 7 for pure and contaminated

water, respectively. It is observed that the collision position increases almost linearly with the initial position,

$$x_{col} = k x_0. \tag{27}$$

Only in the case shown in Fig. 6f, g and h (pure water, higher particle velocity and larger bubble sizes), x_{col} reaches a maximum for x_0 close to 6 mm. At this maximum, the bubble collides with the particle close to its equator. When x_0 is further increased, the bubble still collides with the particle, but this collision occurs in the particle's upper hemisphere. The collision position x_{col} then decreases with x_0 . The collision in the upper hemisphere is probably driven by reversed flow in the recirculation; deeper analysis is, however, difficult because of the unsteady character of this flow.

Results of the model also indicate almost linear dependence of x_{col} on x_0 . In fact, the proportionality constant k is not truly constant, but for the moderate particle velocities considered here, it decreases slightly (at most by 1%) when x_0 is varied from a small value (bubble initially close to the axis) toward a maximum value, at which the collision occurs. In Figs. 6 and 7, the value of k computed from the model is provided and the corresponding dependence is shown by line. The present model fails for x_0 above the its maximum value (colliding in the upper hemisphere of the particle), because of the invalid assumption of the irrotational flow.

The parameter *k* characterizes the bubble deviation from its vertical path caused by the flow around the particle. It primarily depends on the particle velocity, bubble size and mobility of bubble surface. The last two parameters determine the bubble terminal velocity. In Fig. 8, the computed parameter *k* is plotted against the ratio of particle and bubble terminal velocity, U_p/U_b . Obviously, the values computed for both particle velocities (50 and 100 mm/s) and for both pure and contaminated liquid fall on a single master curve, demonstrating that the velocity ratio is an important dimensionless parameter controlling the collision process between small bubbles and large particles.

The linear dependence of x_{col} on x_0 and the dependence of the factor k on the velocity ratio U_p/U_b are consistent with the model of Flint and Howarth (1971). Note that x_{col} is linearly proportional to x_0 also in the frame of Sutherland's model (1948), but the values of k are inconsistent with it. For convenience, a combination of both models is provided in Appendix A.



Fig. 5. Example of experimental dataset on bubble velocity. Dependence of relative bubble velocity on time to collision. The particle diameter 14.11 mm, particle velocity 50 mm/s, bubble diameter 0.5962 mm, bubble terminal velocity 137.6 mm/s, and pure water.



Fig. 6. Dependence of the bubble collision position on the initial position. Pure water, particle settling velocity 50 mm/s (a-d) and 100 mm/s (e-h).

4.3. Flotation efficiency

In mineral flotation (small particles collected on a larger bubble), the efficiency is defined as the ratio of particles, attaching to a bubble, divided by the total number of particles in the volume swept by the bubble.

The collision, attachment and also possible detachment are usually considered as independent sub-processes (Derjaguin and Dukhin, 1961) and the flotation efficiency is then the combination of the efficiencies of all individual steps. Here, we focus only on the collision process. Its efficiency is defined as the ratio of the number of colliding particles to



Fig. 7. Dependence of the bubble collision position on the initial position. Contaminated water, particle settling velocity 50 mm/s (a-d) and 100 mm/s (e-h).



Fig. 8. The dependence of parameter k on the ratio of particle and bubble terminal velocity, U_p/U_b .

the total number of particles in the swept volume. In the present case of plastics flotation, the configuration is inverted (small bubbles are collected by a larger moving particle). The collision efficiency E_c can be defined analogously as the ratio of number of bubbles colliding with the particle to the number of bubbles that would collide, if their trajectories are not deflected by the flow around the particle. Similarly to the case of mineral flotation (see e.g. Nguyen and Schulze (2004)), this efficiency can be determined from the bubble grazing trajectory (with initial position $x_{0,g}$), which distinguishes the trajectories of bubbles that encounter the particle surface from those that do not. Based on a simple geometric interpretation of the grazing trajectory, one obtains for the bubble–particle collision efficiency

$$E_c = \left(\frac{x_{0,g}}{R_p + R_b}\right)^2 \approx \frac{1}{k^2}.$$
(28)

The latter's approximate equality can be used, if the parameter $k = x_{col} / x_0$ is independent of x_0 , hence $x_{0,g} \approx (R_p + R_b) / k$. This holds reasonably for the conditions studied here.

The resulting collision efficiency is summarised in Fig. 9, where the efficiency is plotted against the velocity ratio U_p/U_b . Black points are the results of the presented model, using which the position $x_{0,g}$ of grazing trajectory was determined and the efficiency evaluated using Eq. (28). Compared to the experiments, the set of data was enlarged to cover the range of particle velocities from 5 to 200 mm/s, bubble diameters from 0.4 to 0.8 mm and both mobile and immobile bubble surfaces. Despite this relatively large range of particle velocities, all the efficiencies follow a single master dependence on U_p/U_b , as seen in Fig. 9.

Nowadays in mineral flotation, the gravitational, interception and inertial mechanisms of bubble–particle collision are usually considered (Nguyen and Schulze, 2004; Dai et al., 2000). The gravitational mechanism assumes that the velocity of particle differs from that of liquid due to particle settling, and consequently particle trajectories deviate from the streamlines of the liquid flow around the bubble. This deviation is characterized by the ratio of velocities of the bubble rise and particle settling. The impact of this mechanism on the efficiency of mineral flotation was derived first by Flint and Howarth (1971). Following their approach for the plastic flotation (see also Appendix A), one obtains for the efficiency due to the collisions driven by the bubble buoyancy

$$E_{c-FH} = \frac{U_b/U_p}{1 + U_b/U_p}.$$
 (29)

This efficiency is shown in Fig. 9 by the dark solid line. This simplified model underestimates the efficiency especially at larger velocity ratio U_p/U_b , but still it is in a reasonable agreement with the results of the full computational model.

In the case of mineral flotation, the interception mechanism (Sutherland, 1948) assumes that the particle centre follows the liquid streamlines in the bubble neighbourhood. Some streamlines get to the bubble surface to a distance smaller than the particle radius, and the particles travelling along these streamlines collide with the bubble. The Sutherland's reasoning can be repeated for the case of plastics flotation (Appendix A), leading to an analogue of Sutherland's expression for the collision efficiency due to interception

$$E_{c-SU} = \left(1 - \frac{R_p^3}{\left(R_p + R_b\right)^3}\right)^{-1}.$$
 (30)

The efficiency hence increases with the size of captured bubbles. When both the gravitational and interception mechanisms are combined, the overall efficiency is (Appendix A)

$$E_c = 1 - (1 - E_{c-SU})(1 - E_{c-FH}), \tag{31}$$

which is in agreement with the combination rule for individual efficiencies, recommended by Nguyen and Schulze (2004). This combined



Fig. 9. The dependence of collision efficiency on the ratio of particle and bubble terminal velocity, U_p/U_b .

efficiency is shown in Fig. 9 by the dotted line. The interception mechanism modifies only slightly the collision efficiency, which is mostly governed by the bubble buoyancy. Inclusion of the interception improves the estimation of collision efficiency, but still the real efficiency is higher (the difference amounts to 5% for $U_p/U_b \approx 5$).

The remaining difference is attributed to the inertial forces. In the mineral flotation, the particle inertia is important for heavy and/or large particles and becomes dominant for Stokes number greater than unity. Due to the inertia, sufficiently massive particles are unable to follow the liquid motion along curved streamlines and tend to follow the previous movement. In the case of plastics flotation, the inertial effects are quite different. The bubble itself has no inertia, and all inertial effects are linked with the liquid motion. The liquid motion has two origins: due to i) the bubble motion relative to the surrounding liquid, and ii) liquid motion around the falling particle. The liquid inertia due to the bubble motion opposes the changes of the relative velocity between the bubble and the surrounding liquid via the added-mass force \mathbf{F}_{am} . The inertial effects due to the liquid motion around the particle lead to the inertial force F_{I} , which drives the bubble in the direction of decreasing pressure. Combining both effects, the inertia act on the bubble in the opposite sense than it would on a particle heavier than the liquid: the bubble decelerates faster than the liquid when it approaches the particle on axis (heavy particles would move faster than the liquid in this zone), and close to particle equator, the inertial forces due to streamline curvature push the bubble toward the particle surface (heavy particles would be pushed away because of centrifugal forces).

Anyway, owing to moderate values of the Stokes number, the efficiencies predicted by the full model, which includes inertial effect (symbols in Fig. 9) are relatively close to the simplified model that neglects the inertia (Eq. (31), dotted line in Fig. 9). This suggests that the inertial forces have only moderate impact for studied conditions, and can be neglected in many practical applications. When the simplified model is compared with the results of full model, it is also observed that for small velocity ratios, $U_p/U_b < 0.5$, the inertial forces lead to a slight decrease of the flotation efficiency. Contrary for $U_p/U_b > 1$, inertial forces increase the efficiency in most cases, mostly due to attraction of the bubble to the particle in the region around equator of the particle. An attempt to quantify the impact of inertial effects on the efficiency was done, but no simple relation was found. Our next effort will be therefore focused on a general model for collision efficiency, which would include the effects of buoyancy, interception and inertia.

Finally, we briefly discuss the importance of individual forces on the resulting bubble motion. The lift force is negligible for any initial positions of the bubble. For bubbles with its initial position far from the grazing trajectory ($x_0 \ll x_{0,g}$), the added-mass force becomes important in the close vicinity of the particle, roughly when the distance between bubble and particle surface is smaller than 5 mm because the added-mass coefficients derivatives (Eq. (18)) increase significantly. Bubbles with initial position close to the grazing trajectory ($x_0 \sim x_{0,g}$) collide with the particle bellow the particle equator. These bubbles follow the S-shaped trajectory (see Fig. 4). As the bubble approaches the particle, it is first deflected off-axis because of the drag force \mathbf{F}_d and inertial force \mathbf{F}_I . When the bubble passes behind the inflection point of liquid streamlines, \mathbf{F}_I becomes the dominant force and drives the bubble toward the particle surface.

5. Conclusions

The collision of a small rising bubble with a larger spherical particle falling through a stagnant liquid is studied. A theoretical model describing the bubble trajectory and velocity evolution is given and its results are successfully validated by comparing with experimental measurements. For both mobile and immobile bubble surfaces, the horizontal deflection of the bubble trajectory prior to the collision increases linearly with the initial bubble distance from the axis. The proportionality factor increases with the ratio of particle and bubble rise velocities and its values are consistent with the model of Flint and Howarth (1971). The collision efficiency is evaluated by determining the grazing trajectories using the present model. The overall efficiency is controlled mostly by the buoyancy of the bubbles, and only partially by the interception mechanism and inertial effects. A simple expression for the efficiency, considering the combined effect of the buoyancy and interception mechanisms, is provided.

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Appendix A. Simplified model for bubble motion

In this Appendix, a combination of models of Flint and Howarth (1971) and of Sutherland's (1948) is provided for the convenience. Size proportions typical for plastics flotation (small bubbles rising around a large falling particle) are considered. This simplified model hence describes the gravitational and interception mechanisms of the capture of small bubbles on a large particle, assuming that effects of inertia on the bubble motion can be neglected.

The potential flow around the spherical particle is considered. The stream function for the potential flow around a sphere is given in Eq. (2), and the velocity components can be determined via (3); note that the system of reference moves together with the moving particle. The bubble rises through the liquid. In the approach of Flint and Howarth (1971), the inertial forces acting on the bubble (\mathbf{F}_{I} , \mathbf{F}_{am} and \mathbf{F}_{L}) are neglected. The bubble consequently moves with a velocity, which differs from that of the liquid, and this difference is constant and equal to the velocity of rise U_b (cf. Eq. (7), and see also Flint and Howarth's solution for his $K \rightarrow 0$). The bubble motion then can be described by a bubble trajectory function ψ_b , which is an analogue of the stream function (ψ_b is constant along bubble trajectory). The trajectory function ψ_b differs to the flow stream function ψ by a term assuring constant vertical velocity U_b , that is

$$\psi_{b} = \psi + \frac{1}{2}U_{b}x^{2} = \frac{1}{2}\left(U_{p} + U_{b}\right) \left[1 - \frac{R_{p}^{3}}{\left(1 + \frac{U_{b}}{U_{p}}\right)r_{b}^{3}}\right]x^{2}.$$
 (A1)

The bubble trajectory function is hence the same as a stream function of a potential flow with velocity $U_p + U_b$ around some ghost particle with diameter $R_p / (1 + U_b/U_p)^{1/3}$. The velocity components of the bubble can be evaluated analogously to (3).

From ψ_b , the dependence of the collision position x_{col} on the initial position x_0 can be determined. During its motion, the bubble follows its trajectory and ψ_b is hence constant. Following the approach of Sutherland, the collision occurs when $r_b = r_{col} = R + R_b$. By writing $\psi_{b,0} = \psi_{b,col}$ and considering the infinite initial radius, $r_0 \rightarrow \infty$, one obtains a relation (27) between the initial and collision positions, and the value of parameter k is

$$k = \left[1 - \frac{R_p^3}{\left(1 + U_b/U_p\right) \left(R_p + R_b\right)^3}\right]^{-\frac{1}{2}}.$$
 (A2)

Considering $U_b = 0$, the simplified model presented in this Appendix reduces to the classical model of Sutherland (1948). Considering $R_b = 0$, the model reduces to that of Flint and Howarth (1971). Compared to these classical models, only the quantities related to the bubble and particle are interchanged as a consequence of inverted proportions in the case of plastic flotation.

With the use of (28), the flotation efficiency of the combined model is

$$E_{c} = 1 - \frac{R_{p}^{3}}{\left(1 + U_{b}/U_{p}\right)\left(R_{p} + R_{b}\right)^{3}} = 1 - (1 - E_{c-SU})(1 - E_{c-FH}), \quad (A3)$$

where the efficiencies E_{c-SU} and E_{c-FH} are efficiencies of Flint– Howarth's and Sutherland's models considered independently, given in (29) and (30).

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The shape of non-axisymmetric bubbles on inclined planar surfaces



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HIGHLIGHTS

- ADSA-P modification for bubbles
- adhering to an inclined solid surface.Contact angles on lower and upper bubble parts are described separately.
- Very good agreement of calculated and experimental data was obtained.
- The method could improve description of TPC line expansion.

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ABSTRACT

Bubble-particle interaction is a common phenomenon that is used in numerous industrial applications, and the knowledge of contact angles is important for the description of the expansion of the three-phase contact line. In contrast to drops, the capture of bubbles adhering to a solid surface is an extremely rapid process, and the image quality that can be achieved is worse. For bubble adhesion on a slightly inclined plane, different curvature radii should be considered on the upper and lower bubble sections of the three-phase contact line. The method proposed here is based on the assumption that the ADSA-P approach could be used separately for both bubble parts.

Bubble motion during the adhesion process was recorded using a high-speed digital camera, and points located on the bubble boundary were detected using image analysis. The bubble was divided into two independent parts, and the ADSA-P technique for contact angles of greater and less than 90° was applied to describe the bubble shape.

The calculated coordinates of the bubble profile were compared to the experimental data, and an excellent agreement was obtained. The proposed methodology could improve and simplify the description of bubble-particle interactions on non-horizontal surfaces.

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1. Introduction

Contact angles have been a subject of interest in both pure and applied sciences. Contact angles are also used to characterize the wettability of materials in many industrial applications. The broad relevance of this topic has led to a great deal of development in measurement techniques. The overwhelming majority of these techniques is focused on the description of the shape of a sessile liquid drop and on the measurement of the contact angle of a drop placed on a horizontal, flat, and homogeneous surface. The simplest "direct" method involves aligning a tangent with the sessile drop profile at the point of contact with the solid surface. A summary of other conventional techniques may be found in more detailed reviews [1]. During the last few decades, the incorporation of computer tools has led to the development of new methodologies. In the present day, methods such as ADSA (axisymmetric drop shape analysis) and APF (automated polynomial fitting) enable the measurement of contact angles with a reproducibility of $\pm 0.2^{\circ}$ [1].

The first axisymmetric drop shape analysis was conducted by Bashforth and Adams [2]. They tabulated drop profiles for liquids with various surface tensions and radii of curvature at the drop apex. Since that time, the methodology has undergone constant

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improvement, and computer calculation of the drop profile has been adopted. In general, ADSA methods provide a contact angle by finding a numerical axisymmetric solution of the Young-Laplace equation with given experimental parameters (drop volume, density, diameter, height, capillary length, etc.) and then calculating the slope of the tangent to the drop surface at the liquid-solid-vapor interface line. Huh and Reed [3] developed the methodology for describing the profile of a drop with a contact angle of greater than 90°. Rotenberg et al. [4] developed a powerful technique called ADSA-P (axisymmetric drop shape analysis-profile), which fits points of the experimental profile to a theoretical Laplacian curve using a nonlinear procedure. The objective function is the sum of the squares of the normal distances between the measured points and the calculated points; one of the independent variables of the objective function is the coordinates of the origin (the drop apex). Skinner [5] modified the basic ADSA method into the ADSA-CD (contact diameter), which is based on the measurement of the contact diameter of the drop from the top view. This method is suitable for drops with contact angles of less than 20° for which other methods fail. Cheng [6] improved the ADSA-P method by introducing the automatic digitalization of images. He incorporated image pre-processing into the ADSA procedure. Finally, del Rio [7] summarized the ADSA-P method for the calculation of contact angles of greater and less than 90°, thereby developing the second generation of ADSA methods, which utilize more efficient algorithms, e.g., using the curvature at the apex instead of the radius of curvature and using the angle of vertical alignment as an optimization parameter. Prokop et al. [8] used the ADSA-P method to study a captive bubble after the equilibrium state was reached. This method is often recommended for liquids or solutions with a low surface tension, in which case the classical pendant drop method fails. At present, a great deal of effort is also being dedicated to the improvement of image quality and analysis [9].

APF (automated polynomial fitting) methodology utilizes new tools of high-resolution image analysis. The contact point is captured in detail, and the drop shape is described using a suitable polynomial fitting module. This technique can also be used for non-axisymmetric drops. The drawback of this technique is the necessity of recording high-quality images with detailed resolution close to the contact point. For example, the method of Chini and Amirfazli [10] is based on the sub-pixel polynomial fitting principle, in which points along the bubble edge are replaced with a polynome. According to the authors' conclusions, an excessive increase in the number of pixel points beyond the plateau region could result in an error in contact angle estimation because of the polynomial's inability to trace the drop boundary shape.

At present, the development of more precise experimental techniques for determining the liquid drop profile and the growing demand for probing smaller scales or achieving quicker processes require the development of novel numerical methods that can go beyond the axisymmetric approximation for the shape of a drop. An important application is the description of the drop or bubble shape on an inclined plane. In 1979, Brown et al. [11] described the shape of a static drop on a tilted surface using the finite element method. The finite element method was also used by Iliev [12,13] for the general description of a sessile drop shape. The goal of this method is to determine the shape and the local contact angles along the contact line for an a priori contact line, volume, and capillary length. The equilibrium drop shape forms as a result of the influence of the surface tension and gravitational forces. The surface is described as Laplacian and minimal. Rotenberg et al. [14] have used the finite element method to predict the shape of a drop slowly sliding down a sloping plane. They described the boundary conditions along the contact line in the form of a functional relationship between the contact angle and the velocity of the three-phase line. Other authors have dealt with the shapes of critical drops, e.g., the

determination of the maximum drop volume. Nguyen [15] has suggested predicting the critical drop volume based on the knowledge of receding and advancing contact angles. El Sherbini [16,17] has developed a method for drop-shape approximation on a tilted plane using two circles fitted to the drop contour line. This method is used primarily for the estimation of the contact angle of critical drops. Finally, Dupont and Legendre [18] have introduced a novel numerical macroscopic-scale method based on the implementation of a sub-grid description of the contact line that relies on imposing an apparent angle for static and moving contact lines.

All the methods mentioned above were proposed primarily for the description of sessile axisymmetric or non-axisymmetric drops. Although, the descriptions of both drop and bubble shapes are based on the same theoretical background; the literature concerned with the description of bubble shape in various industrial applications is scarce. Flotation, which is an example of an important separation method, is based on the ability of certain solids to remain attached to the bubble interface. Flotation was originally used for the separation of coal or mineral ore particles from mined ore deposits. Currently, it is also used for waste-water treatment and for the separation of oil sands, print inks in paper recycling and various plastic materials; in the latter case, the bubbles are smaller than the solid particles. Bubble attachment to a solid surface is the fundamental process of bubble-particle interaction. The attachment process begins with the drainage and rupture of the liquid film between the bubble and the particle, and it continues with the establishment and enlargement of the three-phase contact (TPC) line until its equilibrium state is reached. The contact-line expansion can be described using mathematical models such as the hydrodynamic and molecular-kinetic models [19,20]. Both models relate the dynamic contact angle to the TPC line velocity, and knowledge of the time dependence of the contact angles is essential for the TPC-velocity and TPC-diameter calculations. For a small bubble adhering to a horizontal plane, Phan [19] considered the bubble shape to be spherical. In such a case, the contact angle can be calculated using a simple mathematical relation that describes the intersection of a plane and a sphere. However, this assumption is inapplicable for larger deformable bubbles adhering to a horizontal or even an inclined plane.

When images of a sessile drop and a sessile bubble are compared, the quality of the bubble image is usually lower. This is because the experimental apparatus is more complex. Bubble adhesion is captured using a high-speed camera, which requires a powerful light source. The light rays penetrate through the vessel material and the liquid bulk, so light reflection at both the solid-liquid and gas-liquid interfaces must be considered. Therefore, the analysis of the image data of the area near the three-phase contact point is accompanied by an increase in experimental error, and the application of the APF method is not recommended.

The aim of this project is to design a new methodology for the relatively simple and rapid calculation of bubble contact angles. The method proposed here is based on the assumption that the ADSA-P method can be used separately for two (upper and lower) bubble sections of differing curvature radii.

2. Theoretical description of the bubble shape on horizontal and inclined planes

The process of bubble adhesion on an inclined plane is illustrated in Fig. 1, together with the time information. The moment of threephase-line establishment was defined as the zero time. Because of prior bubble motion along the plane and bubble inertia, the bubble's center of gravity moves forward, and then the bubble center oscillates around its equilibrium position. Initially, bubble adhesion is characterized by a rapid increase in the contact angle. Not



Fig. 1. Sequence of photos showing bubble adhesion to a plane with an inclination angle of 20°. The bubble diameter is 0.44 mm.

long afterward, the contact angle increases slowly until the equilibrium contact angle θ_{eq} is reached. In contrast with a drop placed on an inclined plane, the bubble appears nearly spherical throughout the entire adhesion process, and the differences between the upper θ_u and lower θ_l contact angles are small. In classical terminology, where contact angles are conventionally measured through liquid, the bubble's upper contact angle θ_u would be described as the advancing angle, and the lower contact angle θ_l would be the receding angle. In pure water or dilute aqueous solutions, the bubble size is close to the bubble capillary length *a*, which is defined as $a = (\gamma/(\rho_l - \rho_g)g)^{0.5}$. Here, ρ_l denotes the liquid density, ρ_g denotes the gas density, and γ denotes the liquid's surface tension. Under the above-mentioned conditions, surface forces are expected to exert an important influence.

Because of plane inclination, different curvature radii should be considered on the upper and lower bubble sections of the TPC line. For small inclinations, the bubble remains nearly spherical, and the difference $\theta_u - \theta_l$ does not exceed 5°. We assume that it is possible to divide the bubble into two independent parts. Each part is assumed to be axisymmetric and can be described using the ADSA-P technique. The bubble is divided using a straight line that is perpendicular to the inclined plane and intersects the bubble surface at its most distant point. A schematic illustration is provided in Fig. 2. This condition is later set as a boundary condition. The bubble is observed from the side view, and a two-dimensional description is considered. Points located on the bubble boundary are detected via image analysis. The ADSA-P technique differs for bubbles with contact angles of greater or less than 90°; therefore, both approaches are described below.

2.1. ADSA-P method for a bubble with a contact angle of less than 90°

This procedure was originally proposed for drops with contact angles of greater than 90° [3] and could also be used for bubbles with contact angles of less than 90°. The calculation is based on the Laplace–Young equation, which describes the pressure difference across a curved interface. It is convenient to write equations for the bubble shape in a Cartesian system with two dimensionless variables *x* and *y* in terms of the slope angle of the meridional curve, $\varphi = \tan^{-1}(dy/dx)$:

$$\frac{dx}{d\varphi} = \frac{\cos\varphi}{y + \frac{2}{h^{0.5}} - \frac{\sin\varphi}{x}}$$
(1)



Fig. 2. Scheme of bubble separation into two independent parts.

$$\frac{dy}{d\varphi} = \frac{\sin\varphi}{y + \frac{2}{\mu_0 5} - \frac{\sin\varphi}{x}}$$
(2)

$$x = rc^{0.5} \tag{3}$$

$$y = zc^{0.5} \tag{4}$$

$$b = \beta^2 c \tag{5}$$

The initial conditions are x(0) = y(0) = 0. Here, x and y are dimensionless coordinates, r and z are real coordinates, b and c are parameters, and β is the initial bubble curvature. A schematic illustration of the bubble profile is provided in Fig. 3A. The calculation is performed sequentially, and the value of parameter b is gradually increased throughout. For each step, the objective function R is determined:

$$R = \sum_{i=1}^{n} d^{2} \left[(r_{i}, z_{i}), \left\{ r(b, c), z(b, c) \right\} \right]$$
(6)

After a local minimum of *R* is reached, the new value of parameter *c* is calculated.

$$c^{0.5} = x_e / r_e \tag{7}$$

The procedure continues until the objective function is minimal. Finally, the resulting curve that best fits the experimental data is selected. In Eq. (6), index *i* denotes the experimentally obtained points. In Eq. (7), the index *e* indicates a location on the equator (the point on the bubble edge corresponding to $\varphi = 90^\circ$). Finding the coordinates for $\varphi = 90^\circ$ and the related calculation of the "new" parameter *c* is a very important step in ensuring that the curve is "attached" correctly at this point and that the final contact angle is less than 90° .

2.2. ADSA-P method for a bubble with a contact angle of greater than 90°

The mathematical description of a bubble with a contact angle of greater than 90° follows the Rotenberg method [4]. The calculation is once again based on the Laplace–Young equation. The model is defined by a system of equations with dimensionless variables *x* and *y* (the horizontal and vertical directions, respectively), and the independent variable is the arc length *s*. A schematic illustration is provided in Fig. 3B.

$$\frac{dx}{ds} = \cos\varphi \tag{8}$$

$$\frac{dy}{ds} = \sin\varphi \tag{9}$$

$$\frac{d\varphi}{ds} = 2 + by - \frac{\sin\varphi}{x} \tag{10}$$

$$x = \frac{r}{\beta} \tag{11}$$

$$y = \frac{z}{\beta} \tag{12}$$



Fig. 3. ADSA-P method for a bubble with a contact angle of less than 90° (detail A) and greater than 90° (detail B).

$$s = \frac{S}{\beta} \tag{13}$$

$$b = \frac{\left(\rho_l - \rho_g\right)g\beta^2}{\gamma} \tag{14}$$

The initial conditions correspond to the origin, i.e., $x(0) = y(0) = \theta(0) = 0$. As in section 2.1, x and y are dimensionless coordinates, r and z are real coordinates, b is a parameter, and β is the initial curvature radius. The subsequent calculations are performed following a procedure similar to that described above. Parameter b is changed, and the objective function is determined; the calculation is finished when the objective function is minimal.

3. Experimental

The experimental measurements were performed in a glass flotation cell (5.5 cm in height, 8 cm in width, 6 cm in depth). Single bubbles with diameters from 400 to 700 µm were created using a bubble generator built following the design of Vejražka [21]. After undergoing free motion in a stagnant liquid, the bubble collides with the solid surface. A glass slide was placed on a prism with a horizontal or inclined plane (inclination angle of 10°, 20°, or 30°). The glass was silanized using dimethyldichlorsilan, (CH₃)₂SiCl₂ (Sigma–Aldrich, Silanization solution I). According to Zisman's method, the solid surface energy γ_{sg} of the silanized glass was 23.1 mN/m. The experiments were conducted in pure distilled, de-ionized, and de-mineralized water at 26 °C. The surface tension of the water was 71.6 mN/m, its pH value was 6.13, and its conductivity was 1.6 µS/cm. An equilibrium contact angle of 97.8° was measured using the ADSA-P technique for a sessile water drop on this surface.

Bubble motion prior to the collision with the solid particle and during adhesion was recorded using a high-speed digital camera (Redlake Motion Scope M2; 2000 fps, resolution of 1280×256 pixels, calibration of the optical system $2.44-4.94 \,\mu$ m/px) with a Navitar macro objective. For each sequence, between 500 and 1000 frames were collected. The image-analysis software NIS-Elements was used for the detection of point coordinates around the bubble. The original image was thresholded, and a reference image with a marked inclined plane was added. After overall contour detection, part of the inclined plane was subtracted, and the bubble contour was obtained along with the coordinates of each pixel. Further calculations were performed using MATLAB software.

4. Results and discussion

A typical experiment is illustrated in Fig. 1. The adhesion of a bubble with a diameter of 0.44 mm to a plane with an inclination angle of 20° is depicted here. The entire sequence consists of 560 images; here, only a few images are selected. After the rupture of the thin liquid film (defined to be at zero time), TPC line expansion accompanied by a rapid increase in the contact angle was observed. After 0.1 s, equilibrium had nearly been achieved. The sequence was interrupted after 0.3 s. At this time, the bubble shape was stable, and the upper and lower contact angles did not change for more than 0.1 s. The bubble profiles that correspond to the original images shown in Fig. 1 are plotted in Fig. 4. Because of the camera rotation, the plane seems to be horizontal. In fact, the inclination angle was 20°, and the lowest point on the bubble contour corresponds to the most distant point, where the bubble was separated into two parts. The experimental data obtained using image analysis are represented as points. Shape oscillations, which can be seen in Fig. 4 as varying distances of the bubble boundary points from the symmetry axis, are visible at a time of 1 ms; after 15 ms, it can be observed that equilibrium had almost been achieved. The ADSA-P method was applied separately for both parts of the bubble, and the



Fig. 4. Bubble profiles at selected times. Comparison of experimental (points) and calculated (lines) data. The inclination angle of the plane was 20°, and the bubble diameter was 0.44 mm.

Table 1

Summary of experimental equilibrium upper contact angles θ_u , lower contact angles θ_l , differences $\Delta \theta = \theta_u - \theta_l$, experimental diameters of the three-phase contact line d_{TPC} , calculated theoretical angles θ_{sphere} , calibration and variation.

d _b (mm)	Plane inclination	0°	10°	20°	30 °
0.44	θ_{upper} (°)	94.7	92.8	87.2	81.8
	θ_{lower} (°)	94.6	93.9	88.4	83.8
	$\Delta heta$ (°)	-0.1	1.1	1.2	2.0
	d _{TPC} (mm)	0.590	0.581	0.552	0.529
	θ_{sphere} (°)	97.3	95.6	89.5	84.7
	Calibration (µm/px)	2.69	2.43	2.20	2.71
	Variation (µm)	4.21	4.21	3.88	4.70
0.56	θ_{upper} (°)	93.8	94.8	76.6	88.0
	θ_{lower} (°)	93.7	96.0	78.3	89.6
	$\Delta heta$ (°)	-0.1	1.2	1.7	1.6
	d _{TPC} (mm)	0.751	0.738	0.703	0.662
	θ_{sphere} (°)	97.3	95.2	89.6	82.9
	Calibration (µm/px)	3.02	3.03	2.69	2.69
	Variation (µm)	5.31	5.70	5.37	4.74
0.63	θ_{upper} (°)	94.5	98.1	88.7	88.7
	θ_{lower} (°)	94.6	99.0	90.0	90.4
	$\Delta heta$ (°)	0.1	0.9	1.3	1.7
	d_{TPC} (mm)	0.842	0.829	0.787	0.752
	θ_{sphere} (°)	97.0	95.1	89.1	84.0
	Calibration (µm/px)	3.48	3.02	3.47	4.05
	Variation (µm)	5.21	5.37	5.21	7.18

contact angles were calculated. The calculated data are depicted in Fig. 4 as lines. The agreement between the experimental and calculated data is very good. The method was also tested on a water drop placed on the inclined plane with an inclination of 15° . Using the suggested method, the advancing contact angle was found to be 70.1° , and the receding angle was 52.0° . These data were compared to the direct measurements, from which we obtained 70.9° for the advancing angle. The agreement is very good.

The equilibrium contact angles and statistics for both horizontal and inclined planes are summarized in Table 1. The upper and lower contact angles (θ_u and θ_l , respectively) and the difference $\Delta \theta = \theta_u - \theta_l$ were calculated as average values over more than 3 bubbles. For each bubble, at least 300 images were used for this statistical processing. The contact angles calculated for the initial stage of bubble adhesion were not considered for the statistical treatment. Furthermore, the average variation for the entire sequence is listed alongside information regarding the optical calibration. The variation was calculated as follows:

variation =
$$\frac{1}{n} \sum_{i=1}^{n} \sqrt{(r_{i,exp} - r_{i,teor})^2 + (z_{i,exp} - z_{i,teor})^2}$$
 (15)

Here, *n* is the number of experimental points around the bubble edge. The experimental equilibrium diameter of the three-phase contact line d_{TPC} is listed, as well. These diameters were obtained using the image-analysis software. This diameter was used for the calculation of the theoretical contact angle θ_{sphere} under the assumption of a strictly spherical bubble shape. The spherical cap that represents the adhered bubble and has the same volume as the bubble can be described as a portion of a sphere cut off by a plane. The diameter of the cap's base is than equal to d_{TPC} .

According to Young's equation, on horizontal and flat surfaces, the equilibrium contact angles on opposite sides of the bubble should have identical values. This condition was fulfilled. With increasing plane inclination, the upper and lower contact angles (θ_u and θ_l , respectively) decrease significantly. The values fluctuate slightly for different bubble sizes. Inconsistent data were obtained for $d_b = 0.56$ mm ($\alpha = 20^\circ$) and $d_b = 0.63$ mm ($\alpha = 10^\circ$), which we attribute to different wettabilities or roughnesses of the prepared solid surfaces. According to the theoretical assumptions, for the considered bubble diameters, the influence of the bubble size

should not be significant. It should be necessary to consider such a correction only for large drops, for which gravity forces should be dominant over surface forces. In general, the difference $\Delta \theta = \theta_u - \theta_1$ increases with increasing plane inclination. The average difference reaches 2° for an inclination angle of 30°. In fluid mechanics, the capillary length *a* characterizes the mutual relation between the gravitational/buoyancy acceleration and the surface force due to the liquid surface tension. For clean water and air at standard temperature and pressure, a is approximately 2 mm. A capillary surface whose largest dimension is much smaller than the capillary length will take the shape of a spherical cap, which is the solution to the Young-Laplace equation when buoyancy is completely neglected. For bubbles with diameters from 0.5 to 0.9 mm, the influence of surface forces is dominant over the influence of gravity, but the omission of buoyancy is not justified. The difference between the obtained equilibrium contact angle $\boldsymbol{\theta}$ and the theoretical angle $\theta_{\rm sphere}$ on the horizontal surface demonstrates the necessity of taking buoyancy into account. For inclined planes, the Young-Laplace equation is not valid, and the influence of the buoyancy force on the upper bubble edge is increased.

In the case of an inclined plane, the decrease in the contact angles is related to the decreased diameter of the three-phase line. The experimental contact angles (both θ_u and θ_l) differ significantly from the theoretical angles calculated for an absolutely spherical bubble cap. The maximum difference is 6°. Based on the obtained results, it is found that it is insufficient to approximate the bubble shape with a sphere and to assume equal contact angles for all plane inclinations.

According to the data in Table 1, the variation increases slightly with increasing bubble size. In fact, the sum of squares in Eq. (15) is dominated primarily by a calculation error that arises close to the three-phase contact point. The number of experimental points increases during bubble adhesion. The average maximum number of experimental points is 50 points for a small bubble and 60 points for a large bubble. The variation ranges from 4 μ m for small bubbles to 5–6 μ m for large bubbles and does not exceed the experimental error, which corresponds to 1.5–2 pixels. We believe that this accuracy is sufficient. More precise contact angles might be obtained if the image quality were to be increased.

The method described above is focused primarily on the description of the shape of a bubble during its adhesion on a solid surface. In Fig. 5, the time evolution of the contact angle is illustrated for



Fig. 5. The time dependence of the contact angles for plane inclinations of 0°, 10°, 20° and 30° and a bubble diameter of 0.44 mm.

a bubble with a diameter of 0.44 mm. Data for bubble adhesion on a horizontal plane (circles) and on planes with inclination angles of 10° (triangles), 20° (squares), and 30° (rhombi) are summarized here. The data depicted here belongs to a single experimental set, but the obtained contact angles do not differ significantly from the average values calculated from data obtained for at least four bubble-adhesion sequences. For the horizontal plane, the data are relatively smooth. A bubble in a stagnant liquid rises with a fairly rapid velocity, and after collision with the solid surface, single or even multiple bubble rebounds are observed. This rebound is accompanied by bubble oscillations, which are primarily in the vertical direction. The oscillations are symmetric, so their influence on the contact angle is relatively minor. After a sufficiently long time (approximately 60 ms) the bubble motion decreases, and the contact angle is close to its equilibrium value. When the bubble moves along an inclined plane, the establishment of the TPC line is again very rapid, and this process is accompanied by the motion of the bubble's center of mass in the direction of its previous movement. Therefore, we observe bubble oscillations in the planes both perpendicular and parallel to the solid surface. The parallel motion has a significant influence on the contact angles. This influence is apparent in Fig. 5, where for times smaller than 70 ms, the values of the upper and lower contact angles oscillate. For times greater than 100 ms, the bubble shape remains almost stable, and only insignificant changes in the contact angles are observed. The differences $\Delta \theta = \theta_u - \theta_l$ are clearly visible, but they do not exceed 4° in the rapid phase of the TPC expansion. Close to the equilibrium, the difference reaches a maximum of 2°.

Similar results were also obtained for larger bubbles with a diameter of 0.63 mm. Selected data for a horizontal plane and plane



Fig. 6. The time dependence of the contact angles for plane inclinations of 0° and 20° and a bubble diameter of 0.63 mm.

of inclination 20° are presented in Fig. 6. The time scale is extended up to 150 ms. A larger bubble is more affected by oscillations, which is clearly visible in the case of the horizontal plane, where the contact angle in the beginning of the slow adhesion phase varies periodically. The oscillations are suppressed after approximately 100 ms. According to Zedníková [22] and Vejražka [23], the frequency of such oscillations is subject to meaningful interpretation, and it can be described using mathematical models. During bubble adhesion on an inclined plane, the bubble shape changes irregularly. The differences $\Delta \theta = \theta_{11} - \theta_1$ are significant, and in some cases, they are as large as 6° in the rapid phase of TPC expansion. For one such specific case, we attempted to use the classical ADSA method for the description of the shape of the entire bubble, but the calculation did not converge. The contact angles were also measured manually using the direct method, and the data agreement was very good. In fact, the application of the direct method is unsuitable for sequences that contain up to 1000 images; it was used only as a comparative method. The bubble oscillations were found to be nearly suppressed after 100 ms, and after 150 ms, the bubble was found to achieve and retain its equilibrium shape. Similar results were obtained for the plane with an inclination of 30°.

5. Conclusion

The description of the shape and contact angles of a bubble adhering to a slightly inclined solid surface is essential for the description of the expansion of the three-phase contact line. Although the bubble appears nearly spherical, an approximation of a strictly spherical bubble cap leads to incorrect contact angles. When compared with experimental results, this difference can be as large as 6°. The classical methods based on ADSA methodology consider an axisymmetric bubble shape, but this requirement is not fulfilled on inclined planes. The method proposed here is based on the assumption that the ADSA-P approach could be used separately for the upper and lower bubble sections, which have different curvature radii of the TPC line. The difference between the equilibrium upper and lower contact angle increases with increasing inclination angle and reaches 2° for an inclination of 30° . In the rapid phase of bubble adhesion, the difference can be as large as 6° because of non-symmetric bubble oscillations. Each time, the calculation of the contact angles converged; a very good agreement between the calculated and experimental contact angles was obtained. The accuracy is consistent with the experimental error. Therefore, the proposed method could improve and simplify the description of bubble-particle interactions on non-horizontal surfaces.

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Technical note The collision efficiency of small bubbles with large particles

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ABSTRACT

Bubble–particle interactions play an important role in many technological processes, e.g., in flotation. Although mineral flotation involves fine particles, this work focuses on the interactions between a small bubble and larger spherical particle and determining their collision efficiency. Based on the theoretical and experimental work, a simple relation for estimating the collision efficiency is proposed. The calculated efficiencies are compared to a large set of experimental data and are found to be in excellent agreement.

 $E_{\rm c} = 1 - (1 - E_{\rm b})(1 - E_{\rm s})(1 - E_{\rm i}).$

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1. Introduction

Particle-bubble interactions are a central issue in physicochemical hydrodynamics, surface forces, multiphase reactors and the dynamics of wetting films and adsorption at liquid interfaces. The mechanisms of bubble-particle interactions also control the selectivity and efficiency of the flotation process (Dai et al., 1998). Flotation is based on the ability of some solids to remain attached to the bubble surface, and thus, the efficiency expresses the probability that the bubble and particle will make contact and become strongly attached. The basic principles of flotation are currently utilized in many other industrial applications, such as the separation of waste plastics (e.g., Fraunholz, 2004; Pascoe, 2005), where interactions between small bubbles and large particles are considered.

For a bubble to capture a hydrophobic particle efficiently, they must first undergo a sufficiently close encounter. A number of excellent reviews on determining the collision efficiency in mineral flotation mostly consider the gravitational, inertial and interception mechanisms (Nguyen and Schulze, 2004; Dai et al., 2000). The collision efficiency E_c is then given by:

$$E_c = 1 - (1 - E_g)(1 - E_s)(1 - E_i).$$
(1)

Here, E_g , E_s and E_i denote the efficiencies due to gravity, the interception mechanism and inertia, respectively. When a small bubble – large particle interaction is considered, a similar description can be utilized. The efficiency due to the bubble buoyancy E_b replaces the gravity mechanism, and the E_c relation can be rewritten as:

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liquid, particles have a certain settling velocity and therefore their trajectory deviates from fluid streamlines. This deviation may cause particles to collide with the bubble surface (Miettinen et al., 2010). For a Stokes number approaching zero, efficiency due to the gravity mechanism E_g could be expressed by the relationship between the particle velocity U_p and bubble velocity U_b (Flint and Howarth,1971):

$$E_g = \frac{U_p}{U_b + U_p}.$$
(3)

Simultaneously for bubbles, the efficiency due to the buoyancy mechanism E_b is defined as:

$$E_b = \frac{U_b}{U_b + U_p}.\tag{4}$$

The collision of particles with the bubble surface by interception is due to a flow which carries particles along the fluid streamlines. The particles come into contact with the bubble surface because of their finite size. For mineral flotation, Sutherland (1948) used this conception to lay the foundations for most of the relations for the collision efficiency. This reasoning can also be used for interactions between small bubbles and large spherical particles, leading to an analogy of Sutherland's expression for the collision efficiency due to interception:

$$E_{s} = 1 - \frac{8D_{p}^{3}}{\left(2D_{p} + 2D_{b}\right)^{3}}.$$
(5)





(2)

MINERALS ENGINEERING In mineral flotation, the inertial mechanism was often neglected. This mechanism becomes dominant when the Stokes number is greater than unity. In real flotation systems with intermediate Stokes numbers, modern theories such as GSE (Dai et al., 2000) consider both positive and negative inertial forces. For potential flow, less complex models are preferred. Following expression for the inertial efficiency E_i is recommended (Nguyen and Schulze, 2004; Langmuir and Blodgett, 1945):

$$E_i = \left(\frac{St_b}{St_b + 0.5}\right)^2.$$
(6)

The Stokes number St_b for a rising bubble near a large settling particle is defined as:

$$St_b = \frac{4}{9} \frac{\rho_l D_b^2 U_p}{\eta_l D_p}.$$
(7)

Recently, the collision process between a small rising bubble and larger spherical falling particle was studied experimentally and theoretically (Hubička et al., 2013). The published theoretical model, which is based on an analysis of the forces acting on the bubble, includes a differential equation for the bubble motion and thus allows the bubble trajectory and velocity to be described. In this work, we add new experimental data for a larger particle and we focused on establishing a simple relation for estimating the collision efficiency. The results are compared to a large experimental data-set that includes varying particle sizes, settling velocities, bubble sizes, rising velocities and bubble surface mobility.

2. Experimental

Experiments were performed at 25 °C in pure water (de-mineralized, surface tension 71.6 mN/m) and in an aqueous solution of the surface active agent terpineol (Fluka Company, concentration 187 mg/l, surface tension 63 mN/m). The particles were smooth, spherical glass balls with diameters of 14.1 mm and 19.8 mm. The experimental measurements were collected in a glass cell (details in Hubička et al., 2013). Single bubbles were created using a bubble generator. The bubble-particle interactions were observed with a Redlake Motion Pro high-speed camera (500 fps), which was fixed to the translating unit moving parallel with the particle. The particle size, particle velocity (50 and 100 mm/s; controlled by computer), bubble surface mobility (pure and contaminated water) and bubble size ($D_b \sim 0.5$ –0.8 mm) were varied between the different data sets. The images were analysed using NIS-Elements software, by which the bubble size, bubble centre position and collision point were determined. Altogether, 32 sets of experimental data were obtained. For each experimental set, the trajectories from at least ten bubble initial positions were measured.

3. Results

The flotation efficiency is defined as the ratio of the number of colliding particles to the total number of particles in the swept volume. In the present case of plastics flotation, the relative sizes of the bubbles and particles are switched. The collision efficiency E_c can be defined analogously as the ratio of the number of bubbles colliding with the particle to the number of bubbles that would collide if their trajectories were not deflected by the flow around the particle. Similar to the case of mineral flotation (e.g., Nguyen and Schulze, 2004), this efficiency can be determined from the bubble grazing trajectory (with initial position $x_{0,g}$), which distinguishes the trajectories of bubbles that encounter the particle surface from those that do not. Based on a simple geometric interpretation of the grazing trajectory, the bubble–particle collision efficiency is:

$$E_c = \left(\frac{2x_{0,g}}{D_p + D_b}\right)^2 \approx \frac{1}{k^2}.$$
(8)

The parameter k characterizes the deviation of the bubble from its vertical path, which is primarily due to the liquid flow around the particle. This parameter was measured experimentally. On condition that the frame of reference moves together with the particle and its origin is fixed in the particle's centre, the horizontal position of the bubble centre in its initial position (sufficiently distant from the particle) can be defined as x_0 and simultaneously the position of the bubble centre at the collision point can be characterized by its horizontal position, x_{col} . Then parameter k is defined as:

$$\kappa_{col} = k x_0. \tag{9}$$

The linear dependence was confirmed both experimentally and theoretically (Hubička et al., 2013). The approximate equality in Eq. (8) can be used if the parameter $k = x_{col}/x_0$ is independent of x_0 ; hence, $x_{0,g} \approx (D_p + D_b)/2k$. This assumption was confirmed for the conditions considered here.

All the experimental results, including D_p , D_b , U_p , U_b and E_c , calculated according to Eq. (8) are summarized in Table 1.

In mineral flotation, the collision efficiency is relatively low. Dai et al. (2000) compared all significant theoretical models to the

Table 1

Survey of the experimental collision efficiencies E_c with their corresponding particle diameters D_p , settling velocities U_p , bubble diameters D_b and terminal velocities U_b .

		Mobile bubble surface			Immobile bubble surface		
D_p (mm)	U_p (m/s)	$D_b (mm)$	$U_b(\mathbf{m/s})$	E _c	$D_b (mm)$	$U_b(m/s)$	E _c
14.1	0.050	0.500	0.105	0.71	0.553	0.064	0.60
14.1	0.050	0.596	0.142	0.78	0.618	0.073	0.64
14.1	0.050	0.709	0.184	0.84	0.694	0.082	0.67
14.1	0.050	0.798	0.231	0.87	0.803	0.094	0.71
14.1	0.100	0.515	0.110	0.56	0.473	0.054	0.39
14.1	0.100	0.622	0.145	0.65	0.580	0.067	0.46
14.1	0.100	0.731	0.195	0.73	0.691	0.080	0.51
14.1	0.100	0.806	0.233	0.77	0.785	0.092	0.54
19.8	0.050	0.492	0.099	0.69	0.508	0.057	0.61
19.8	0.050	0.640	0.151	0.74	0.617	0.072	0.65
19.8	0.050	0.689	0.172	0.77	0.681	0.079	0.66
19.8	0.050	0.818	0.219	0.81	0.748	0.088	0.67
19.8	0.100	0.479	0.098	0.51	0.494	0.059	0.45
19.8	0.100	0.603	0.138	0.60	0.583	0.073	0.48
19.8	0.100	0.706	0.186	0.65	0.670	0.078	0.52
19.8	0.100	0.805	0.231	0.69	0.741	0.087	0.53



Fig. 1. Dependence of the collision efficiency E_c on the relative velocity ratio U_b/U_p .

experimental data. For example, the experimental E_c is 10% when $D_b = 0.77$ mm and $D_p = 0.0006$ mm. The interception mechanism is known to be the predominant one whereas the influence of the gravity mechanism is insignificant. When small bubbles and large particles interact, the situation is completely different and the probability of collision is high.

The parameter k characterizes the bubble deviation from its vertical path caused by the flow around the particle. It primarily depends on the particle velocity, bubble size and mobility of bubble surface. The last two parameters determine the bubble terminal velocity. If the parameter k is plotted against the ratio of terminal bubble and particle velocity (U_b/U_p) we obtain a single master curve. It demonstrates the importance of the velocity ratio as the dimensionless parameter controlling the collision process between small bubbles and large particles (Hubička et al., 2013). This linear dependence is consistent with the buoyancy model (Eq. (4)).

In Fig. 1, all the experimental and theoretical data are summarized. The dependence of the collision efficiency E_c on the ratio $U_b/$ U_p is illustrated. The experimental efficiencies listed in Table 1 are depicted as circles and rhombi. Data for bubbles with mobile or immobile surface mobility are differentiated in the plot. The efficiencies calculated using the theoretical model (Hubička et al., 2013) are illustrated with squares. The efficiency calculated using Eq. (4) is shown as the full black line. It is obvious that the Flint-Howarth buoyancy model, expressed using the ratio U_b/U_p , represents the experimental data up to $U_b/U_p \cong 0.4$ perfectly but underestimates efficiencies for lower values. The accuracy could be improved provided that the interception and inertia mechanisms are included. Results are illustrated in Fig. 1 as crosses. Here, E_c was calculated according to Eq. (2), where E_b , E_s and E_i were calculated using Eqs. 4, 5, and 6 respectively. The agreement with experimental data is evident.

Based on this large data-set, we attempted to summarize the data and find a general, simple relation for a quick estimation of collision efficiency. Based on the regression analyses, we obtained the following equation:

$$E_c = \frac{U_b/U_p}{1.02568 \ U_b/U_p + 0.74057}.$$
 (10)

This relation is valid for $U_b/U_p \ge 0.40$. The efficiencies calculated using Eq. (10) are illustrated with a full grey line. The coefficient of determination $R^2 = 0.99946$ indicates very good agreement between the estimated and experimental data. In the velocity ratio range $U_b/U_p \in \langle 0.40, 25 \rangle$, the verified data exist; the average error is 2.4% and the maximum error is 8.2%.

The suggested relation is also suitable for a lower velocity ratio $U_b/U_p < 0.40$, but the agreement might be worse. In this region, the influence of inertial forces increases. Similar to the GSE model (Dai et al., 2000), the theoretical model includes both positive and negative inertial forces. These forces become important close to the particle equator having a substantial influence on the collision efficiency and as a consequence efficiencies calculated using both Eqs. (10) and (6) are lower in this region.

4. Conclusions

The collision of a small rising bubble with a larger spherical particle settling through a stagnant liquid was studied to determine the collision efficiency. A simple estimation equation was proposed based on a large experimental dataset and on efficiencies calculated using a theoretical model. The agreement between the estimated efficiencies and experimental or calculated efficiencies is very good.

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Bubble-particle collision interaction in flotation systems



OLLOIDS AND SURFACES A

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HIGHLIGHTS

- Particle trajectories and particle–bubble collisions observed experimentally.
- Model developed to describe particle trajectories around single bubble.
- Comparison between experimental and theoretical particle trajectories.
- Assessment of effects influencing bubble-particle interaction: gravity, inertia, microhydrodynamic drag.

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GRAPHICAL ABSTRACT



ABSTRACT

This work studies single bubble–single particle interactions of interest to flotation applications. An experimental device has been developed where a standing bubble is approached at prescribed flow velocity by an aqueous dispersion of particles – much smaller than the bubble. Two separate high-speed cameras are employed to monitor the bubble surface from two different Cartesian directions allowing thus a 3D perspective of particles trajectories and collisions with the bubble. A special feature of the device is that the velocity of the suspension and the size of the bubble can be independently adjusted in a range of values that corresponds to the flotation process. This paper presents experimental trajectories and velocities of particles as they approach and flow past a bubble. A theoretical model has been developed to describe such particle trajectories and velocities. Comparison between experimental observations with model predictions allows a detailed assessment of governing forces and better understanding of their contribution to particle–bubble interactions. It is shown that microhydrodynamic drag has a distinct role in matching experiments with predictions.

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1. Introduction

Interaction between solid particles and air bubbles in aqueous solutions is of academic and practical significance. It is a typical process in nature, but it also plays an important role in several industrial applications. Flotation is one of these applications in which bubble–particle interactions constitute a key process; flotation is a separation method used in the recovery of coal and valuable minerals from ores [1], in the removal of pollutants from waste waters [2], de-inking of paper in recycling of wastepaper [3], recovery of plastic mixtures in recycling plastic waste [4], etc. Flotation is often employed to separate hydrophobic from hydrophilic particles in an aqueous suspension by introducing air bubbles into the suspension. After attaching to air bubbles, hydrophobic particles are dragged upwards by rising bubbles and form a froth at the top of the suspension [1,5].

Although flotation is known for very long time, a systematic analysis of the governing sub-processes has attracted attention the last 50 years only. The main individual elementary steps of flotation are (a) collision of a solid particle with a bubble, (b) attachment of a

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particle to a bubble and (c) detachment of a particle from a bubble. Proper description of these steps is essential for the determination of the efficiency of the flotation process and the determination of its kinetics [1,6]. Understanding and thus controlling the interaction between colliding particles and bubbles has proved very important to achieve successful attachment of particles onto bubbles [7].

Bubble-particle encounter includes many kinds of interactions and forces - hydrodynamic, gravitational, surface and capillary. The three identified sub-processes (collision, attachment, detachment) are not entirely discrete, but rather grade one into another [7]. However, the governing forces are independent of each other so collision, attachment and detachment can be treated separately and thus modelling of each sub-process is simplified. The collision sub-process starts already from the approach of a particle to encounter a bubble that is governed by the liquid flow and the relative motion between the bubble and the particle. Particle/bubble trajectories determine whether an encounter will occur. Collision is dictated by the zonal boundary between long-range hydrodynamic forces and short-range interfacial interactions. It is only when a particle approaches a bubble at a shortest separation distance that short-range forces (atomic, molecular, surface) take control, and the attachment process starts [8]. Collision efficiencies are usually computed through trajectories calculation. Although the trajectory calculation is an old issue in flotation modelling [1], only recently microhydrodynamics has been incorporated in this [7,9].

In past studies of bubble–particle collision, bubbles with immobile surface have been mostly considered on the premise that surfactants and impurities adsorb on a bubble surface making it immobile [1,10]. In recent years, however, research has turned also on a collision of particles with mobile bubble surfaces [10–12]. The argument for this is pretty clear: adsorption of surfactant at the surface of a rising air bubble is a dynamic process, contaminants are swept to the rear surface of the bubble and thus, the forward part of the bubble remains mobile, whereas the surface contamination forms an immobile stagnant cap at the rear [13].

Only a few attempts have been reported in the literature aiming to investigate isolated bubble-particle collision and attachment. In most of these studies, a bubble is pinned at the tip of the capillary, and its surface is recorded by a high-speed camera while it is approached by particles settling inside a stagnant liquid [7]. Such experiments do not consider liquid flow so particles collision with the bubble is determined solely by particles settling velocity. A few, more ambitious, attempts employed a moving high-speed camera that can follow in real time the rising motion of a bubble in stagnant liquid [12]. The latter is much closer to a real flotation situation, e.g., DAF tanks, but it proved extremely difficult to track a rising bubble and at the same time keep its surface in focus. Slight lateral motion of the bubble and inevitable hydrodynamic disturbances are enough to drive images out of focus.

This work is about experimental trajectories and local velocities of small spherical particles flowing around a large spherical bubble. The presently reported trajectories/velocities are those of relatively large particles - still smaller than the bubble - that move chiefly under gravitational settling. In order to describe particle trajectories/velocities a theoretical model has been developed incorporating the effects of governing forces, e.g., gravity, inertia, microhydrodynamic drag. Reynolds numbers of the liquid flow ranks to intermediate values and thus it is not possible to use either Stokes or potential flow for its description. The improvement in flow field description (composite flow) field is also presented in this paper. It is noted that the model developed here is not the main scope of the present work, but it is a tool for the explanation of experimental data. Despite this, the model is a state-of-the-art since for first time, particle trajectories are calculated including hydrodynamics for the flow field different from the two idealized ones (Stokes and potential flow).



Fig. 1. Schematic of the experimental set-up with the detail of the injection device.

2. Experimental

The apparatus used in this project is the opposite of conventional flotation apparatuses; instead of having many bubbles rising through dispersed particles floating freely in the liquid, the situation is simplified and reversed. A single bubble is kept at a fixed position, and the suspension of particles moves against it. The bubble is created at the tip of a vertical capillary tube of external diameter of $600 \,\mu\text{m}$. To make the bubble two syringes are used - one small and one large - connected to the capillary tube by a three-way valve in order to enable manipulation of bubbles size. The large syringe is used to blow a bubble out of the capillary initially, whereas the small syringe is used to adjust the bubble size at a desired level. The three-way valve is also connected to a pressure transducer to monitor the internal bubble pressure by which the system's stability is assessed. Connecting the bubble, the three-way valve, the syringes and the pressure transducer by small diameter (1 mm) short length tubes increase the stability of the system but diminish its dynamic response to pressure fluctuations.

The approaching velocity of particles to the bubble is adjusted by a pump in combination with a control valve. Particles are dispersed in water inside a small reservoir where the desired amount of particles, surfactant and liquid are mixed. Right after mixing, the suspension is pumped through narrow tubes (diameter 5 mm, to maintain particles in suspension) to the top of a vertical glass column (1.5 m height overall) having a large square cross-section ($4 \text{ cm} \times 4 \text{ cm}$). As the suspension enters the glass column the cross-section of the flow increases largely and so the flow velocity decreases drastically. In addition, the flow passes through a bundle of narrow tubes (10 cm long, 2 mm diameter) meant to damp swirling motion of particles and excessive liquid eddies. The ensuing smooth flow moves downwards against the bubble fixed at location 3 (Fig. 1). This is the location where particle trajectories around the bubble are registered by two highspeed cameras (Motion BLITZ EoSEns Mini2, RedLake MotionScope, 500 fps) shooting simultaneously from perpendicular directions. The two cameras configuration permits capturing bubble/particle activities in every direction. Sufficient cold diffuse lighting is employed to illuminate the bubble and approaching particles so as to use high aperture values that increase the depth of view field.

After going past the bubble, the suspension enters a big Plexiglas tank at the bottom of the apparatus where an axial impeller maintains particles in suspension for the pump to re-circulate them. The overall view on the device is shown in Fig. 1. The total volume of the device is 8.61; the length of the column from its top down to location 3, is 1 m.



Fig. 2. Spherical particles of polystyrene crosslinked with divinylbenzene (Micropore Technologies Ltd.) as observed by a microscope.

The experiments shown in this work are performed using spherical hydrophobic particles (polystyrene crosslinked with divinylbenzene, (Micropore Technologies Ltd.) with an average diameter $d_p = 330 \,\mu$ m, $\rho_p = 1050 \,\text{kg/m}^3$, $U_s = 3.1 \,\text{mm/s}$). Although the average size of particles is 330 μ m, particle sizes are distributed in a finite range of values (Fig. 2). Therefore, in the calculations that follow the actual size of each particle is used as recorded by the cameras. The test liquid is an aqueous solution of surface active agent (SDS, sodium dodecyl sulphate) at a concentration of 50 mg/l. This concentration is typical for flotation processes and is considered enough to make particles hydrophobic [1,14]. The presence of surfactants has a significant influence on the bubble surface. Nevertheless, for sizes of bubbles used during the experiments shown

in this paper and the very low concentration of surfactant used, the surface of the bubble is usually considered mobile. The bubble in the presence of the SDS solution of the concentration used shows the partially immobile surface according to Krzan and Malysa [15] who used the solution of SDS of similar concentrations. The same conclusion may be also deduced from the comparison of the terminal bubble velocity; it ranks to the area of the partially immobile surface as provided in [16].

The bubble was formed just exactly before taking the video of the interaction and due to the motion of the liquid, surfactants that could attach to the bubble surface were swept to the rear of the bubble and thus, its surface remained practically clean with the Marangoni effect not being strong enough to alter the velocity field around the bubble. The mobility of the bubble surface was checked by the evolution of the velocity in dependence on the position as seen in Fig. 7.

Video sequences of particles colliding with bubbles of different diameter ($500-1700 \mu m$) under different flow rate (liquid velocity in the column 0–8 mm/s) are obtained. An example is shown in Fig. 3.

The image analysis software NIS-Elements is used for the detection of particle trajectories. Original sequences are represented by images in the .bmp format; it enabled to cut unnecessary images (images with no particles) and then to create a video in the desired format (.nd2). The calibration of distances on images is based on the diameter of the capillary (600 μ m), the bubble with the capillary is marked and excluded from the range of interest. Videos are thresholded and using methods of image analysis, the position of the centre of the particle in every image is obtained. These positions characterized by the *x*- and *y*-coordinates are measured and exported for the following calculations. The velocity is calculated from the trajectory as the change of the particle position as a function of time (the time difference between two images is 2 ms).



Fig. 3. The interaction between a spherical particle and the bubble observed by the high-speed camera. Images represent a sequence separated by 40 ms.



Fig. 4. Illustration of the interaction of a falling particle and a stagnant bubble.

During the present experiments, collision of particles with the bubble is observed at different flow regimes but adhesion of particles on the bubble surface is never observed. This is most likely due to the low SDS concentration. However, such low SDS concentration was necessary to study particles trajectories around a mobile bubble surface which is indeed the scope of our work.

3. Theoretical

3.1. Equations for the particle motion

The quantification of particle–bubble collision outlined in Fig. 4 requires solving the full equation of particle motion around the bubble surface. Successful modelling of particle motion enables the calculation of bubble–particle collision angle and also of the encounter efficiency. Traditionally, it begins with the Basset–Boussinesq–Oseen (BBO) equation described as [1,13]

$$m_p \frac{d\vec{V}}{dt} = m_f \frac{D\vec{W}}{Dt} - 6\pi\eta R_p (f_i \vec{V} - f_j \vec{W}) - \frac{m_f}{2} \frac{d(\vec{V} - \vec{W})}{dt} + (m_p - m_f)\vec{g}$$
(1)

Here, m_p is the particle mass, m_f is the mass of fluid volume occupied by the particle, R_p is the particle radius, V and W are velocities of the particle and the fluid flow (resp.), η is the liquid viscosity, t is time and g represents the acceleration due to gravity.

The term on the left-hand side of the BBO (Eq. (1)) represents the particle inertia forces, the first term on the right-hand side is referred to as the pressure force and the second term as the viscous drag force. The third term is called the added mass force and represents the resistance of the liquid volume decelerating with the particle motion. The last term on the right-hand side of Eq. (1) represents the difference between the particle weight and the liquid buoyancy [9,17–19].

For easier handling of the BBO equation, dimensionless values are introduced by dividing the appropriate dimensional values by their characteristic values. Fluid and particle velocities are scaled by the bubble slip velocity U (difference between fluid and bubble velocity); time is scaled by R_b/U (R_b – bubble radius). This way, dimensionless numbers are obtained under the assumption that the liquid velocity and viscosity are constant; K_1 and K_2 describe the role of inertial forces, where *St* is the particle Stokes number [17].

$$K_1 = \left(1 + 0.5\frac{\rho_f}{\rho_p}\right)St\tag{2}$$

$$K_2 = 1.5 \frac{\rho_f}{\rho_p} St \tag{3}$$

$$St = \frac{2R_p^2 U\rho_p}{9\eta_f R_b} \tag{4}$$

In Eqs. (2)–(4), ρ_f and ρ_p denote liquid and particle densities (resp.), *U* is the bubble slip velocity relative to the liquid phase, and η_f denotes the liquid kinematic viscosity.

Due to possible instabilities during calculation with time derivatives (small changes in time can cause considerable changes in the particle polar coordinates), it is more convenient to transform Eq. (1) to polar coordinates, where the polar angle and the radial coordinate are independent variables. The particle velocity in radial and tangential direction is defined as (τ is the dimensionless time):

$$\nu_r = \frac{dr}{d\tau} \tag{5}$$

$$v_{\varphi} = r \frac{d\varphi}{d\tau} \tag{6}$$

Then, Eq. (1) can be rewritten as

,

$$\frac{dv_r}{d\varphi} = \left\{ \frac{v_{\varphi}^2}{r} + \frac{K_2}{K_1} \left(w_r \frac{\partial w_r}{\partial r} + \frac{w_{\varphi}}{r} \frac{\partial w_r}{\partial \varphi} - \frac{w_{\varphi}^2}{r} \right) + \frac{f_3 w_r - f_1 v_r - v_g \cos \varphi}{K_1} \right\} \frac{r}{v_{\varphi}}$$
(7)

$$\frac{dv_{\varphi}}{d\varphi} = \left\{ -\frac{v_{\varphi}v_r}{r} + \frac{K_2}{K_1} \left(w_r \frac{\partial w_{\varphi}}{\partial r} + \frac{w_{\varphi}}{r} \frac{\partial w_{\varphi}}{\partial \varphi} - \frac{w_{\varphi}w_r}{r} \right) + \frac{f_4 w_{\varphi} - f_2 v_{\varphi} - v_g \sin \varphi}{K_1} \right\} \frac{r}{v_{\varphi}}$$
(8)

$$\frac{dr}{d\varphi} = r \frac{\nu_r}{\nu_{\varphi}} \tag{9}$$

where v and w represent dimensionless particle and liquid velocities, indexes r and φ denote radial and tangential components of those velocities.

To solve the differential equations showed above, the initial conditions describing the system are required. Their determination is based on the fact that the particle velocity sufficiently far away from the bubble surface is not influenced by the bubble and thus the velocity is equal to the liquid velocity plus the particle terminal settling velocity, giving:

$$v_r(r = r_0) = -(1 + v_g) \cos \varphi_0 \tag{10}$$

$$v_{\varphi}(r = r_0) = (1 + v_g) \sin \varphi_0 \tag{11}$$

The minus sign in the initial condition for the radial velocity (Eq. (10)) denotes that the liquid flow and thus the particle move in counter-current direction to the radial coordinate.

3.2. Microhydrodynamic interaction

A particle approaching the bubble surface is significantly influenced by the drag force which is well described by the Stokes law far from the surface. When the particle approaches the bubble, an intervening liquid film is formed, and the hydrodynamic resistance increases rapidly. This increase can be accounted for using hydrodynamic resistance functions [1,9], f_i and f_j , where i = 1, 2 and j = 3, 4 in Eqs. (7) and (8).

The microhydrodynamic resistance functions depend on the inter-surface separation distance as well as the bubble surface mobility. For mobile bubble surface, equations for the microhydro-dynamic functions in tangential and radial direction are [1]:

$$f_1 = \left[1 + \left(\frac{R_p}{4H}\right)^{0.719}\right]^{1.394}$$
(12)

$$f_{21} = \frac{1.707 + (H/R_p)}{0.836 + (H/R_p)} \tag{13}$$

$$f_{22} = \frac{2.656 + (H/R_p)}{1.440 + (H/R_p)} \tag{14}$$

$$f_2 = \frac{f_{21} - Hf_{22}}{1 - H} \tag{15}$$

$$f_3 = \frac{1.106 + (H/R_p)}{1.502 + (H/R_p)} \tag{16}$$

$$f_4 = \frac{1.107 + (H/R_p)}{1.502 + (H/R_p)} \tag{17}$$

When the bubble and particle surfaces are far apart $(H \rightarrow \infty)$, drag coefficients are equal to 1 and thus, the drag force reduces to the standard Stokes law. On the other hand, when $H \rightarrow 0$ drag coefficients are expressed by the lubrication theory [1].

3.3. Liquid flow field

The Stokes or potential flow describing the liquid flow field has a limited range of successful usage [20,21]. This is why, a significant improvement is introduced here. The composite flow field is able to describe various ranges of liquid velocities (and thus Reynolds numbers). Moreover, it is clearly visible that if a = 0, Eqs. (18) and (19) lead to the Stokes flow. The composite flow field is derived based on the idea of [22] for interpolation between ideal fields.

$$w_r = -\left(1 - \frac{1-a}{r} - \frac{a}{r^2} - \frac{a}{r^3} + \frac{a}{r^4}\right)\cos\varphi$$
(18)

$$w_{\varphi} = \left(1 - \frac{1 - a}{2r} + \frac{a}{2r^3} - \frac{a}{r^4}\right) \sin \varphi$$
(19)

$$a = \frac{4}{45} Re_b^{0.72} \tag{20}$$

3.4. Calculation of the particle trajectory

Equations for the particle motion (Eqs. (7)-(9)) together with the initial conditions (Eqs. (10) and (11)) and equations for the liquid flow field (Eqs. (18) and (19)) are solved in Matlab using the fourthorder Runge–Kutta method. The initial position (r_0 , φ_0) necessary for the calculation is obtained from experiments. In fact, the initial position should be sufficiently far from the bubble where the initial conditions apply and particle trajectories are not influenced by the bubble surface and also they are parallel [17].

In the calculation of the trajectory, the contact of the particle with the bubble is tested (separation distance *H* is equal or smaller than h_0 – see below for its definition). If the particle touches the bubble, the radial motion of the particle is stopped (if it is towards the bubble), and only the tangential one is allowed, and thus, the sliding of the particle along the bubble surface is simulated. When a particle reaches the point corresponding with the tip of the capillary, and the bottom part of the bubble, the motion of the particle is set to follow the shape of the capillary since the flow field disturbance induced by the capillary is not taken into account.

The grazing trajectory, from which the encounter efficiency is calculated, can be found using the condition that there is no contact point between the particle and the bubble surface on the trajectory following the grazing one. The initial position is varied; the particle position corresponding to the particle position obtained from the experiment is initially set to start the numerical integration, and the particle trajectory is calculated [17,18]. If the particle meets the bubble surface (this is detected by fulfilling the condition $r = 1 + h_0/R_b + R_p/R_b$), the integration is stopped, and the initial position is shifted away from the axis of symmetry (the vertical axis). This process is repeated until no contact point is found. Then, the last trajectory is determined to be the grazing one. The angle of tangency is obtained from the grazing trajectory as the polar angle corresponding to the closest point to the bubble surface. The collision efficiency can be calculated from information about the grazing trajectory:

$$E_c = \left(\frac{R_c}{R_b + R_p + h_0}\right)^2 \tag{21}$$

It is important to note that the parameter h_0 representing the shortest inter-surface separation distance (the thickness of the intervening liquid film between the bubble and the particle) is a small number but it is not equal to zero. It was proved [9] that this small non-zero number is sufficient for performing the calculation and moreover, numerical results (collision angle and efficiency) are not sensitive to the value of h_0 that corresponds to typical values for the film thickness (10–500 nm).

4. Results and discussion

Comparison of trajectories of particles going around the bubble obtained experimentally and theoretically is provided in this section. Trajectories of particles passing the bubble at the vertical equator were chosen for further processing. At first, an image summarizing trajectories of particles of different initial position is shown in Fig. 5. These trajectories were obtained from the model by incorporating all effects, and it is provided for better illustration of behaviour of particles. Coordinated *x* and *y* are dimensionless and thus, the bubble ranks between $\langle -1;1 \rangle$. The colour of trajectories differs according to particles initial position; the behaviour of trajectories of the same colour is alike. The agreement between the model and the experiment was checked and expressed by a variation (average distance between calculated and experimental coordinates) giving 1.5 pixels in average (due to the different calibration of images, the pixel size is more relevant information). It



Fig. 5. Trajectories of particles moving around a bubble at different distances from the bubble. Different colours denote particles of different initial positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

is not possible to provide strict statistics since each particle has its own size and initial location (Fig. 2).

For further discussions, single trajectories from the green, red and black zones were used (A, B, C in Fig. 6).

The principle of display of Figs. 6 and 7 must be also introduced here. In both of these figures, the red line denotes results obtained from the experiment, and the green line shows results from calculations. The length of green and red lines is the same for every picture, because the calculation of the particle trajectory was terminated when the horizontal position had reached the value corresponding to the horizontal position of the last point of the experimental trajectory. Since the calculation of the particle velocity is related to the calculation of trajectory, the lengths of the green (calculated) and red (experimental) lines match as well.

According to the initial position of the particle, trajectories showed different behaviour (Fig. 6); for more convenient comparison, axes are provided in a dimensionless form. Particles initially located away from the axis of symmetry deviate around the bubble without coming close (case C); if particles started even further from the axis of symmetry, they would not be affected by the bubble at all, and they would follow streamlines of the liquid flow field. However, if the initial position of particles ranks in the range of the bubble radius from the axis of symmetry, the bubble's presence affects their trajectories significantly (cases A and B). The deviation of the trajectory becomes evident usually at separation corresponding to the diameter of the particle. This can be attributed to forces taking place in the fluid such as drag force, added mass force, inertia force, etc. Some particles sufficiently close to the axis of symmetry slide along the bubble surface and then withdraw. This can be caused by the gravitational effect or the effect of the velocity of the liquid stream. However, particles may also attach onto the surface of the bubble after a short period of sliding, but this case of behaviour is never observed during the shown experiments.

Different trajectories corresponding to different effects used in calculations are depicted in Fig. 6. It must be noted that the present model assumes flow around a perfectly spherical bubble without the presence of the bubble's supporting capillary. From the top to the bottom row, the calculation with all effects incorporated is shown first and then below the calculations without microhydrodynamic drag, without the inertia effect and without the effect of gravity. From A to C, trajectories correspond to different initial

position of the particle; the horizontal initial position divided by the bubble radius is $0.28R_b$, $0.63R_b$ and $0.92R_b$ for A, B and C is shown, respectively.

When comparing experimentally obtained trajectories with those resulting from the equations described in the theoretical part of this paper, contributions of different effects are assessed (microhydrodynamic drag, inertia forces, and gravity effects). Although particles are of relatively large diameters, their density ($\rho_p = 1050 \text{ kg/m}^3$) is similar to the density of the liquid ($\rho_f = 998 \text{ kg/m}^3$), so the influence of inertia and gravity is visible but not so significant. In general, the inertia effect is described by the Stokes number; more significant is the inertia effect, slower the particle reacts to a change of the flow field. The gravity effect expressed via the settling velocity is noticeable if the difference between the particles, the trajectory is almost not influenced by the liquid field and the particle settles vertically.

Contrary assumption, microhydrodynamic drag does not affect the trajectories presented in this work considerably. Without microhydrodynamic effects included in the calculation, the particle approaches the bubble with just a small deviation from the trajectory caused by the liquid flow and the particle collides with the bubble (separation distance, H=0). At this moment, the radial velocity does not contribute to the interaction, and only the tangential velocity causes the further motion of the particle (sliding around the bubble surface). Once the particle reaches the point defined by the capillary and the bottom part of the bubble, it continues in sliding along the surface of the capillary (cases A and B).

If microhydrodynamic effects are incorporated to the calculation, the drag taking place in short inter-surface separation distance "pushes" the particle away from the bubble surface while it is forced by the liquid flow to collide at the same time. It results in the diversion of the trajectory that can be seen in Fig. 5 when trajectories with all effects involved and trajectories without the effect of microhydrodynamics are compared. Also for the case C showing the situation of a particle passing the bubble sufficiently far from the surface where short-range forces do not play a key role and the motion of the particle is controlled by the liquid flow, the effect of the microhydrodynamic is slightly visible.

Next, velocities of particles obtained from experiments and the respective velocities calculated at different locations around the bubble are compared to assess further the significance of different acting forces. In Fig. 7, particle velocities from experiments and calculations are shown for the same cases shown in Fig. 6. For convenience, the horizontal coordinate (showing the vertical position of a particle) in graphs in Fig. 7 is dimensionless (Y/R_b) and thus, the position of the bubble spans within (-1;1) with the centre point in 0; once one want to read in this figure, it is necessary to do it from right to left to follow the motion of the particle. It must be noted that due to imperfections in recorded images, the computed experimental velocity of particles is fluctuating (especially in case A of Fig. 7). It is seen that the velocity of the particle becomes lower as the particle approaches the bubble. When the particle slides along the bubble surface, its velocity initially increases until the equator (centre) plane of the bubble and then, it decreases again as it approaches the bottom of the bubble. The above are consequences of the high mobility of the bubble surface. If the bubble surface is mobile, the velocity is higher around the bubble surface (with the highest velocity at the bubble equator). On the contrary, if the surface of the bubble is immobile, the velocity gets lower along the bubble surface. The obtained experimental velocities indicate that the bubble surface is mobile as it has been assumed based on the employed low SDS concentration. This can be viewed yet from another standpoint: it is possible to judge whether the surface of the bubble is mobile or immobile from knowledge of the local



Fig. 6. Trajectories of particles moving around a bubble in different distances from the bubble surface for different settings of the model. Red lines denote the trajectory of the particle from experiment; green lines are calculated trajectories. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

particle velocity. The main purpose of creating Fig. 7 was checking the bubble surface mobility. However, moreover, it showed its benefits also in decision whether the effect of microhydrodynamics was important or not (for particles moving very close to the bubble surface, cases A and B).

From the comparison of the experimental velocity of the particle with the calculated one, it is possible to examine which of the effects taking place during the bubble-particle interaction are dominant. Although experimental and theoretical trajectories appear quite similar, the velocity counterparts are different for every setting of the model. Cases A and B of the interaction provided in Figs. 6 and 7 show that microhydrodynamic effects must be included in the model. Otherwise, the velocity of the particle when the particle is sliding along the bubble surface is unreasonably high; the only questionable case is C, which represents the particle with the initial position further from the axis of symmetry where microhydrodynamic drag does not take place being a short-range effect.



Fig. 7. Velocities of particles moving around a bubble in different distances from the bubble surface for different settings of the model. Red lines denote the velocity of the particle from experiment; green lines are calculated velocities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Another interesting issue must be pointed on; if the particle slides along the bubble surface (only the tangential motion is allowed), there is a terminal point defined by the tip of the capillary and the bottom of the bubble or the capillary as the lowest possible horizontal coordinate of the particle edge (particle's centre + diameter). From this point further, the radial motion is also allowed, and the particle is forced to slide down along the capillary with the velocity equal to the one in the changing point. This approach geometrically simulates the presence of the capillary – the velocity does not increase again and thus, it represents the immobile surface of the solid capillary.

Although particle attachment to the bubble is possible theoretically under certain conditions, this is not observed during the present experiments. There are a few possible explanations for this discrepancy. A first explanation refers to the morphology of the employed particles. Their surface is perhaps too ideally spherical and too smooth and thus a particle can touch the bubble surface at a point only. This extremely small area of contact may prevent the intervening liquid film between the bubble and the particle from rupture, and as a result, the particle eventually slides away along the bubble [23]. A second possible explanation is that the presence of surfactant increases the intervening liquid film stability or makes the bubble surface immobile [24]. The latter possibility is rather rejected because experimental particle velocities indicate that the bubble surface is mobile. The type and concentration of surfactant (SDS) in the present experiments resemble those of a real

system used in industry (where particles indeed attach onto bubbles), [25]. A third, but least plausible, explanation for the never observed particle–bubble attachment is the weight of the particle; although the density of particles is low, particles are relatively large and thus gravity might be dominant. However, the modelling part of the present work has shown that the effect of gravity is rather insignificant. To this end, the explanation that has more chances to explain the lack of particle-bubble attachment is the first one: particles are too spherical and too smooth to lead a collision with the bubble to eventual attachment.

Another interesting phenomenon observed in the present experiments is that particles continue their motion in an almost straight line after passing the bubble horizontal equator if they did not slide (clearly visible in the case C in Fig. 6). This implies that the effect of gravity or inertia may be dominant, but the present computations showed that none of them is important. The most reasonable explanation for this behaviour is the deformation of the liquid flow field imposed by the presence of the capillary supporting the bubble. This effect has not been considered by the model that is based on the flow field around an isolated bubble.

It is noted that the bubble in general deforms as the particle approach to it [26,27]. This deformation is of the scale of the intervening liquid film between particle and bubble, and it is important for particle attachment process. Nevertheless, attachment does not occur here, and the influence of bubble deformation on particle trajectory is quite insignificant and it can be ignored. The problem has actually three size scales: the bubble size scale (liquid flow field), the particle size scale (relevant to microhydrodynamics) and the intervening liquid film size scale. The bubble deformation and the liquid film thickness evolution can be ignored at the two higher size scales.

5. Conclusions

A new device is developed to yield experimental trajectories and velocities of particles flowing around a bubble standing still in an aqueous surfactant solution. Trajectories and velocities are computed from the analysis of high-speed images. The experimental velocity profiles of particles around the bubble indicate that the surface of the bubble is pretty mobile that is not surprising based on the employed low surfactant concentration. Experimental trajectories and velocities are compared to respective quantities predicted by a model that is also developed herein. A sensitivity analysis reveals that under the experimental conditions interception is the dominant collision mechanism, whereas the other mechanisms has a small but non-negligible effect. However, gravity and inertia gain gradually importance as the size of particles increases and the microhydrodynamic effect increases its importance as the initial position of the bubble's centre is shifted closer to the axis of symmetry. Thus, it can be concluded that the primary mechanism of collision is interception in this case. It is also suggested that the never observed experimentally attachment of particles onto the bubble, despite the favourable physicochemical conditions, is rather due to the specific morphology of the employed particles. These particles are too spherical and too smooth and probably touch the bubble surface at one point only. Therefore, the time and area of the contact are not sufficient for the rupture of the intervening thin film between the bubble and particle.

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Atypical wetting behaviour of alcohol-water mixtures on hydrophobic surfaces



DLLOIDS AN



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Aqueous solutions of alcohols exhibit certain specific properties, such as viscosity maximum or high contact angles.
- These phenomena are caused by a complex inner structure of alcohol-water mixtures.
- The existence of small aggregates consisting of water and alcohol molecules is assumed both in bulk liquid and on interface layers.
- Aggregates are stable over time and influence the surface tension and wettability.

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ABSTRACT

Methanol, ethanol, *n*-propanol and their aqueous solutions are widely used in many industrial applications where wettability is one of the most important parameters. This project was focused on the experimental study of the wetting behaviour of these mixtures on two similar hydrophobic surfaces in the full concentration range. Based on the measurements of dynamic surface tension and dynamic liquid drop spreading we proved the stable composition of liquid layers on the solid–liquid and liquid–air interfaces. Likewise, in bulk liquid the existence of small aggregates consisting of water and alcohol molecules is assumed. This complex internal structure of aqueous solutions of short chain alcohols influences the surface properties of these solutions and explains the higher contact angles when compared to pure liquids with similar surface tension.

> of liquid surface tension, air bubbles adhere onto the particles with lower wettability, promoting flotation, whereas particles hav-

> ing higher wettability will be wetted sufficiently without bubble

attachment. An appropriate substance which is commonly used to

control the surface tension of flotation liquids is an aqueous solu-

tion of a simple alcohol, such as methanol or propanol [1]. Due to the development of new materials and their surfaces, the surface wettability or nonwettability is a very important material property. New materials are developed as hydrophobic, but a small

addition of alcohol or surfactant could change this hydrophobicity

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1. Introduction

Alcohols, along with surface active agents (surfactants), are used in many industrial applications. Flotation of plastics is a good example. Here, waste plastic materials are separated according to their wettability and/or liquid surface tension. At appropriate values

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into hydrophilicity. Water-alcohol mixtures are also widely used and studied due to their important role in biological systems, and pharmaceutical and technical applications. In these applications, alcohols are used both in low concentrations (as co-surfactants) as well as in high concentrations (co-solvents). The systems consisting of alcohols and surfactants are studied with emphasis on adhesion mechanism [2–6], evaporation [7,8], micellar structure and dynamics, etc. Together with this research, experimental studies of the internal structure of aqueous alcohol mixtures are also being carried out. Hydrogen bonding liquids, such as alcohols, have a rich microstructure that the stronger hydrogen bonding water does not seem to possess. It was found that simple alcohols are micro heterogeneous since they tend to develop distinct local microstructures, which are dependent on the geometry of the constitutive molecules such as chainlike structures or micelle like structures. The polarity of water and alcohol self-association as well as cross-association between water and alcohol show significant impacts on physical and chemical properties, like the existence of a viscosity-composition maximum, decrease of partial molar volume or interfacial properties [3,9].

The objective of this paper is to present some new results on the wetting behaviour of alcohol solutions. The project is focused on the experimental study of wetting properties of aqueous solutions of short chain alcohols (methanol, ethanol and *n*-propanol in full concentration range) on two hydrophobic surfaces with similar surface energy. The mutual relationship between liquid surface tension and contact angle is studied and evaluated for aqueous solutions of these alcohols. Together with alcohols, the wetting properties of pure organic liquids and selected aqueous solutions of surface active agents are studied and compared. On behalf of the obtained results, the key properties of aqueous solutions of alcohols influencing the atypical wettability are discussed and evaluated.

2. Contemporary short view on wetting of solid surface

When a drop of a pure liquid is placed on a solid surface, it forms a characteristic shape described by the contact angle θ . In an ideal case, when a horizontal, flat and homogenous solid surface is assumed, Young's equation describes the equilibrium of solid–liquid–vapour interface.

$$\gamma_{\rm SL} = \gamma_{\rm SV} - \gamma_{\rm LV} \times \cos\theta \tag{1}$$

Here, γ_{SV} , γ_{SL} and γ_{LV} correspond to solid–vapour, solid–liquid and liquid–vapour interfacial tension, respectively. γ_{LV} is commonly called the surface tension of the liquid; γ_{SV} is sometimes equated with the surface free energies γ_S [4,10]. Moreover, γ_{SV} is often incorrectly equated with γ_{SG} (solid–gas interfacial tension). This can only be an approximate measure for non-volatile liquids. A deep analysis was given by Siboni [11]. For solid surface characterization, solid tension in a vacuum is often used too. The difference between this tension and γ_{SV} is then called "spreading pressure" π_e .

In Young's equation, only γ_{LV} and θ can be measured experimentally. Values of γ_{SV} and γ_{SL} can only be obtained indirectly. Fundamentally, they reflect the strength of molecular interactions within the bulk material [12]. Then γ_{SL} reflects the cross-interactions between two phases and may be derivable in terms of γ_{LV} and γ_{SV} . Historically, Zisman was the first to formulate what is his fundamental hypothesis of the so-called "critical surface energy γ_C ". This method assumes that the contact angle of a liquid on a solid becomes zero when γ_{SV} and γ_{LV} are equal, and γ_{SL} is reduced to zero. The tension γ_{SV} is hereupon named "surface free energy of solid" [11] and it is denoted as γ_C . Experiments were carried out on fluorinated wax FC721 with a set of 13 organic liquids [13] and the difference $\gamma_{SV} - \gamma_{LV}$ (or $\gamma_{LV} \times \cos \theta$) was plotted against the surface tension of the liquids used. Here, the linear dependence of $\cos \theta$ on

 γ_{LV} was assumed. However, according to recently published studies [11,14], the function $\cos\theta = f(\gamma_{LV})$ is not a straight line in the full range of liquid tensions; the linearity can be assumed only at the lowest surface tensions.

The majority of hitherto published studies have been devoted to the spreading of pure liquids even though in the majority of applications mixtures of liquids are used. The spreading of liquid mixtures is a very complex process depending primarily on its component properties [15]. Owing to their exceptional practical importance, the aqueous solutions of surface-active agents have been studied in detail for decades. When a surfactant molecule is dissolved in water, the free energy of the system increases. The system responds in order to minimize the contact between the surfactant hydrophobic group and the water [16]. As a result, some of the surfactant's molecules are expelled to the system interfaces. The transport processes take place on three interfaces: (i) surfactant adsorption at the inner liquid-solid interface resulting in a decrease of γ_{SI} , (ii) surfactant adsorption on the liquid-vapour interface resulting in a decrease of γ_{SV} and (iii) the transfer from the drop onto the solid-vapour interface just in front of the drop which hydrophilizes the initially hydrophobic surface. Moreover the surface tension gradient on the liquid-vapour interface causes liquid motion inside the drop (Marangoni flow) [17,18]. Due to the advancing transport of surfactant molecules, all mentioned processes are time dependent and the time evolution of the liquid drop spreading is observed [2]. The velocity of the surfactant transport to the liquid-vapour interface can then be studied by using the dynamic surface tension measurement for instance (e.g. maximum bubble pressure method)

The aqueous mixtures of short chain alcohols decrease the surface tension similarly as surfactants and, therefore, both types of mixtures are often equated. However, alcohol solutions exhibit some specific behaviour which depends on their microstructure. Alcohol and water molecules tend to develop the local microstructures in the bulk liquid and, moreover, the existence of a specific saturated microlayer on the solution-air interface is assumed. This internal structure significantly influences the interfacial properties, like surface tension or contact angle.

3. Experiments

3.1. Materials

A silanized glass and PTFE were used as model hydrophobic surfaces. The silanization method is based on the covalent attachment of functional organosilanes to silica or glass. Silanes are believed to react with the exposed hydroxyl groups of silanols on the glass surface and, under optimal conditions, they form a uniform monolayer [19]. In our project, the common type of silanized glass was used: the Silanization solution was supplied by Sigma-Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The silanization method was applied according to recommendations from the literature [19]. The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water and dried. The slides were dipped into the silanization solution for 24 h, then rinsed firstly with pure heptane then with acetone and ethanol in order to remove all organic residues, and finally they were dried. The silanized slides were stored in a dry place to avoid contact with air humidity. The surface homogeneity was tested using the AFM method. On clean glass, the maximum roughness reached a height of 60 nm (average 15 nm), and on silanized glass the maximum roughness reached a height of 160 nm (average 30 nm). The measurement was conducted within 1 week after preparation. Contact angles for pure water ranged from 103.1 to

Table 1

The concentration dependence of surface tension and contact angle of water-alcohol mixtures on silanized glass and PTFE.

Molar concentration (mol/l)	Weight concentration (g/l)	Surface tension (mN/m)	Contact angle on silanized glass (°)	Contact angle on PTFE (°)
Methanol				
0	0	72.2	104.3	104.2
0.011	0.020	68.1	103.6	103.1
0.031	0.054	62.2	100.8	101.2
0.061	0.104	55.9	98.3	98.3
0.092	0.152	51.2	93.4	95.2
0.131	0.212	46.7	91.2	90.9
0.211	0.322	40.5	84.7	85.3
0.341	0.479	35.9	74.8	73.8
0.565	0.698	30.3	62.4	61.4
0.692	0.800	27.9	56.7	56.1
0.762	0.850	26.3	49.9	50.9
0.832	0.898	25.2	43.0	43.6
0.915	0.951	24.1	39.6	38.7
0.960	0.977	23.5	36.5	36.6
1	1	22.0	29.9	30.5
1	1	22.7	23.5	30.5
Ethanol				
0	0	72.2	103.9	104.0
0.008	0.020	63.1	100.9	100.1
0.020	0.050	56.7	96.3	96.8
0.042	0.100	48.9	92.0	92.2
0.065	0.150	43.4	85.9	86.6
0.089	0.199	39.3	80.2	81.0
0.145	0.303	33.3	71.3	71.0
0.279	0.498	29.1	61.2	60.2
0.474	0.697	26.7	51.4	51.8
0.598	0.792	25.7	47.4	48.2
0.680	0.845	25.1	43.9	44.1
0.782	0.902	24.3	41.0	42.2
0.873	0.946	23.5	31.8	32.4
0.935	0.974	23.0	28.3	27.0
1	1	22.6	21.2	20.9
Propanol				
0	0	72.2	103.1	102.3
0.006	0.020	57.0	97.5	96.8
0.015	0.050	45.7	86.3	85.5
0.032	0.100	36.3	76.3	75.2
0.050	0.150	31.1	65.7	67.3
0.070	0.200	28.2	56.9	57.4
0.114	0.300	26.7	52.7	51.9
0.229	0.497	25.9	44.6	46.1
0.413	0.701	25.3	41.7	42.4
0.539	0.796	25.1	38.6	39.2
0.618	0.844	24.9	36.4	35.7
0.732	0.901	24.6	33.1	33.7
0.853	0.951	24.2	27.6	28.0
0.941	0.982	23.9	23.5	24.5
1	1	23.5	20.4	20.6

Table 2

Specification of the set of organic liquids together with their experimental values of surface tension and contact angle at 25 °C.

Compound	Surface tension (mN/m)	Contact angle on silanized glass (°)	Contact angle on PTFE (°)
Acetone	22.8	19.5	21.1
Butanol	24.1	22.8	23.2
Dimethyl-formamide	36.0	60.3	58.2
m-Cresol	36.6	57.9	
Benzylalcohol	39.1	60.7	62.0
Bromoform	39.2	60.0	
Dibenzylamine	39.9	63.2	59.5
Diiodomethan	51.8	84.6	81.6
Glycerol	62.4	94.5	92.5
Water	72.2	104.3	103.2

104.3°. The surface free energy of the solid $\gamma_{\rm C}$ calculated using the set of organic liquids was 21.1 mN/m according to Zisman's method and 21.5 mN/m according to the Siboni approach [7].

Krűss database it ranges from 18.5 to 21.8 mN/m. The wettability of both materials was tested prior each measurement.

Finally, pure but commercial Teflon (polytetrafluoroethylene, PTFE) was used as a second hydrophobic material. Contact angles for pure water ranged from 102.3 to 104.2°. The experimentally measured surface energy of PTFE was 21.2 mN/m; according to the

3.2. Experimental liquids

Pure water (distilled, de-ionised and de-mineralised water) was used at 25 °C for all measurements and in the preparation of aque-



Fig. 1. Surface tension of alcohol–water mixtures. Comparison of experimental and literature data.

ous solutions. The pH value was 6.13 and the conductivity was 1.6 μ S/cm. Pure methanol, ethanol and *n*-propanol with purities of >99.5% were supplied by Penta. Twelve mixtures with water were prepared at 25 °C. Their concentrations in both in mol/l as well as g/l are listed in Table 1.

A set of 10 organic liquids was used for reference measurements. Their list is given in Table 2 together with their surface tension and contact angles. A list of surfactants together with their properties and measured concentrations is given in Table 3. These compounds were supplied by Sigma–Aldrich.

3.3. Experimental methods

The equilibrium surface tension was measured by a tenziometer Lauda TD1 using the Pt/Ir ring tenziometer method (du Nouy's method). The accuracy of the surface tension measurements by this tenziometer was 0.15 mN/m. In all cases, more than 10 successive measurements were performed. The standard deviation did not exceed 0.2 mN/m. Dynamic surface tension was determined by the maximum bubble pressure method using the Krűss BP100 tenziometer. The surface age ranged from 10 ms to 50 s. All experiments were done at 25 °C \pm 0.2 °C.

A Cohu monochrome CCD camera with a $752H \times 548V$ pixel resolution and a Navitar macro-objective were used to capture the drop images with a frame velocity of 15 fps. At least nine drops on three slides were taken for each liquid. NIS-Elements software was utilized for the image processing where the drop profile together with drop height, length and contact angles were analysed. The liquid drop was formed by pumping the liquid using a motor-driven syringe placed in an adjustable holder. The drop volume ranged from 25 to 10 µl so that the drop diameter reached 5 mm. As the drop was forming, the syringe was lifted continuously so that the syringe tip was situated just below the drop surface. Finally the syringe tip was taken out of the liquid. The whole process was recorded and only those images where the drop profile was stable for a sufficient time period were chosen for the analysis. Using this procedure we could eliminate profiles influenced by mechanical imbalances or evaporation. The drop was illuminated from behind using a Schott cold light source. The entire apparatus was mounted on a vibration isolation table, thus minimizing error due to vibrations. Measurements with pure water were done before each set of measurements in order to ensure the stable wettability of the solid surface.



Fig. 2. Dynamic surface tension of pure water (\bigcirc) and aqueous solution of methanol (\Box ; $x_M = 0.131$), ethanol (\Diamond ; $x_E = 0.089$) and propanol (\triangle ; $x_P = 0.070$).

4. Results and discussion

4.1. Surface tension

Experimental surface tension of water-alcohol mixtures in the full concentration range was measured using the du Nouy's ring method and then compared with the published data. A comprehensive set of data measured using the du Nouy's ring method was published by Chodzinska et al. [3]. Besides that, Maximino [20] reported a set of surface tension data measured using the drop volume method, while Glinski et al. [21] and Vasquez et al. [22] measured the surface tensions using the Wilhelmy plate method. Messow et al. [23] published data measured using the maximum bubble pressure method, but only approximate data could be gained from his paper. The drop volume method and the maximum bubble pressure method are dynamic experimental methods; whereas the Wilhelmy plate method and our experimental du Nouy's ring method belong to the semi-static methods. All data are shown in Fig. 1; our experimental values of surface tension are given in Table 1. The accordance of our experimental surface tensions with the above mentioned data is evident. It can also be concluded that the type of experimental method has no influence on the final (equilibrium) value of the surface tension. The observed substantial decrease of surface tension and the non-linear dependence on liquid composition are typical for many binary mixtures. Similar results can be obtained for aqueous solutions of surfactants and even for such mixtures as water-acetone [24].

Dynamic surface tension was measured using the maximum bubble pressure method. Here, the surface tension is measured as a dependent of the bubble surface age. For pure liquids, the surface tension is constant and does not depend on the bubble lifetime. In the case of surfactant solutions the dynamic surface tension decreases. Due to the characteristic molecular structure, surfactants migrate to the liquid-air interphase until their concentration reaches its possible maximum. During this process, surface tension decreases as a function of time (bubble surface age) and finally approaches the equilibrium surface tension. The obtained experimental results for selected mixtures are illustrated in Figs. 2 and 3. Fig 2 gives data for pure water and alcohol-water mixtures with an alcohol weight content of 20%. Full lines represent the surface tension measured using the ring method. The results for surfactant solutions are illustrated in Fig. 3. A slow but constant decrease was observed for ionic surfactants. For non-ionic surfactants, the initial value of dynamic surface tension is similar to pure water and then it decreases with increasing bubble surface age.

The alcohol mixtures exhibit similar behaviour to pure liquids in the sense that the dynamic surface tension is stable over time.

Table 3

Specification of measured aqueous solutions of various surfactants.

Surfactant (abbreviation)	Chemical formula	Туре	Critical micelle concentration (mmol/l)	Measured concentrations (mmol/l)
Dodecyltrimethylamonium bromid (DTAB)	$CH_3(CH_2)_{11}N(CH_3)_3Br$	Cationic	15.3	6.5, 9.7, 13.0, 16.2
Sodium dodecyl sulfate (SDS)	CH ₃ (CH ₂) ₁₁ OSO ₃ Na	Anionic	9.7	5.2, 8.3, 17.3
Octyl phenol ethoxylate (Triton X-100)	$C_{14}H_{22}O(C_2H_4O)_n (n=9-10)$	Non-ionic	0.21	0.1, 0.25, 0.5
Pentaethylene glycol monododecyl ether (C12EO5)	$C_{22}H_{46}O_{6}$	Non-ionic	0.067	0.026, 0.045, 0.055, 0.068, 0.134
Decaethylene glycol monododecyl ether (brij, C12EO10)	$C_{32}H_{66}O_{11}$	Non-ionic		0.0051, 0.0089, 0.016, 0.033, 0.084, 0.160



Fig. 3. Dynamic surface tension of pure water (○) and aqueous solution of SDS (▲, 5.2 mmol/l), DTAB (■, 16.2 mmol/l), C12EO5 (♦, 0.045 mmol/l) and Triton (●, 0.25 mmol/l).



Fig. 4. Contact angles on silanized glass and on PTFE against alcohol molar concentration.

On the liquid–air interface, the existence of a saturated monolayer with a higher alcohol concentration is presupposed when compared with the bulk [3]. The shortest bubble life time during the experimental measurement is 10 ms and even for this short period no change of surface activity was observed. Therefore the concentration of alcohol molecules or aggregates must be stable on this interface. We thus suppose that the creation and saturation of the monolayer is shorter than the bubble life time and the formation of the monolayer does not influence both the bubble or drop behaviour.

4.2. Drop spreading on silanized glass and PTFE

The experimental data describing the dependence of the contact angle on alcohol concentration are given in Fig. 4. It is evident



Fig. 5. Dynamic contact angles of pure water (\bigcirc) and aqueous solutions of methanol (\Box ; $x_{\rm M}$ = 0.131), ethanol (\Diamond ; $x_{\rm E}$ = 0.089) and propanol (\triangle ; $x_{\rm P}$ = 0.070) on silanized glass.

that the surface energy of both measured hydrophobic materials is lower than the surface tension of pure alcohols because contact angles were measured for the full concentration range and none of the solutions spread. The curve shape with two inflexion points is similar to the curve of surface tension. Moreover, the contact angles obtained for both surfaces were almost the same. Identical contact angles for pure water and methanol on PTFE were published by Sefiane et al. [7]. The dependence between the adhesion tension and surface tension is linear for both tested materials ($\gamma_{LV} \times \cos\theta = -0.7724 \gamma_{LV} + 37.25$; $R^2 = 0.9955$). The similarity of contact angles on both surfaces having almost the same surface energy suggests that both of the interfacial energies are similar and the solid–liquid interfacial energy is not influenced by additional forces such as a different electrical charge or an electric doublelayer in the vicinity of the solid surface.

The dynamic wetting was studied for the same solutions in which the dynamic surface tension was measured. In Fig. 5, data are shown for pure water and alcohol–water mixtures with an alcohol weight content of 20%. Full lines represent the average value. The drop image was captured for 60 s. After this period the evaporation effect was visible. Nevertheless no drop spreading was observed and therefore stable alcohol concentration should be expected on both liquid–gas and liquid–solid interfaces. We do not expect a significant influence of the spreading pressure. The spreading pressures are low, for water on PTFE $\pi_s = 9 \text{ mN/m}$ and for propanol $\pi_s = 5 \text{ mN/m}$ [25]. The vapour pressures of water and propanol exhibit similarly low values at 25 °C (close to 3 kPa) and even though the vapour pressure of methanol reaches almost 17 kPa, no significant influence of evaporation on the contact angle was observed.

Fig. 6 presents the results for surfactant solutions. In all cases, drop spreading was observed. This spreading, accompanied by a contact angle decrease, is caused by the more or less fast transport of surfactant molecules to the three-phase contact line. Although the surfactant behaviour in the vicinity of this line is still not



Fig. 6. Dynamic contact angles of pure water (○) and aqueous solution of of SDS (▲, 5.2 mmol/l), DTAB (■, 16.2 mmol/l), C12EO5 (♦, 0.045 mmol/l) and Triton (●, 0.25 mmol/l) on silanized glass.



Fig. 7. The plot of cosine of contact angle (silanized glass in A and PTFE in B) against surface tension.

described in full detail [18], the drop spreading is typical for systems where the concentration of one component on the interface is changing. It could be concluded, based on the measurement of dynamic surface tension and dynamic wettability, that both the bulk and interfacial quantities are constant in the short and medium time periods.

4.3. Combination of surface tension and contact angles

In Fig. 7, the data on surface tension and contact angle are combined together and the cosine of contact angle is plotted against surface tension. Data for the silanized glass surface are illustrated in Fig. 7A and for PTFE in Fig. 7B. The full line illustrates Zisman's method whereby the nearly linear dependence between $\cos \theta$ and γ_{LV} is assumed for pure liquids.

Contact angles of water-alcohol mixtures are much higher when compared with data for organic liquids. The maximum difference reaches nearly 20°. This is evidenced by the contact angle of 57.9° for *m*-cresol (γ_{LV} = 36.6 mN/m) and contact angle of 76.3° for the propanol solution with 0.1 molar fraction (γ_{LV} = 36.3 mN/m). In both cases the drops did not spread and thus the local equilibrium could be considered. Young's equation describes the equilibrium on a solid-liquid-vapour interface and with a simplified approach it can be used for the description of wetting behaviour of nonspreading liquids [26]. Aqueous solutions of short chain alcohols exhibit notable aggregation of their molecules. This internal structure significantly influences both the bulk (viscosity) and interfacial properties (surface tension). This phenomenon is discussed in detail later. Data for surfactant solutions show considerable variance of values which could be caused by imprecise measurement due to the time dependence of both contact angle and surface tension. Nevertheless the contact angles of surfactant solutions are still lower than for alcohols.

4.4. Influence of internal structure of water-alcohol mixtures

Multiple studies by several independent experimental methods demonstrated that short chain alcohols aggregate with water molecules in aqueous solutions. The most comprehensive study was published by Zdziennicka and co-workers [3-6]. Based on the measurement of surface tension, density, viscosity and using the light scattering method they proved the existence of micelle like groupings consisting both of alcohol and water molecules. The viscosity is determined by the interaction between the molecules in the bulk liquid and thus its highest excess viscosity is connected with the strongest coherence of interacting molecules. For all measured alcohols, the viscosity maximum was found for molar concentration between 20 and 30% [3,27-29]. A consistent picture of the molecular organization in the mixture as a function of the composition can also be obtained by using ultrasound propagation and IR spectroscopy. D'Angelo et al. [30] divide alcohol-water mixtures into several types. For very low alcohol concentrations, the solution is essentially monomeric. In the middle concentration region one observes a progressive aggregation of alcohol molecules accompanied by a modification in hydrophobic hydration which is often connected with the existence of clathrate-like structures or micelle-like micro-aggregates. For propanol, the middle region ranges from 0.03 to 0.2 mole fraction. The cluster structure for alcohol-water mixtures was confirmed also by the X-ray scattering technique. Using this technique Takamuku et al. [31,32] confirmed that the structural transition of predominant clusters from the tetrahedral-like structure of water to hydrogen-bonded alcohol chains takes place at $x_{\rm M}$ \sim 0.3, $x_{\rm E}$ \sim 0.2 and $x_{\rm P}$ \sim 0.1, resp. At higher alcohol concentrations ($x_P > 0.7$) the hydrogen-bonded chain clusters predominate.

The viscosity is determined by the properties of the bulk liquid, whereas the surface or interfacial tensions are determined by properties of the appropriate interfacial layer. In solutions of surface-active agents, the surface tension decreases due to the increasing concentration of surfactants in this layer. The surfactant molecules are concentrated in the monolayer and their concentration here is determined by both the surfactant concentration in the bulk liquid and by an ease of transport which is usually expressed using the diffusivity coefficient. A low motion toward the interface was observed for pentaethylene glycol monododecyl ether (see Fig. 3). For surfactants with long, flexible or complex structures, the existence of some adsorption barrier is also expected. This adsorption barrier prevents the monomer from adsorbing. This barrier may be due to increased surface pressure, less 'vacant sites' available for adsorption or there may also be steric restraints on the molecule in the proximity of the interface, and it may have to be in the correct orientation to adsorb [33]. To conclude, surfaceactive agents are adsorbed on the interfacial monolayer gradually and thus the dynamic adsorption and dynamic surface tension are typical for their solutions.

In aqueous solutions of short chain alcohols, alcohol concentrations differ in bulk liquid and on the interface too. For example, the positive alcohol surface excess concentration on the liquid-air interface was guantified and evaluated using Gibbs isotherm [3]. However, the composition of this interfacial layer is stable over time which was proven by dynamic surface tension measurement. Thus it is possible to consider that the molecules located at the interface form also certain aggregates with other molecules in their neighbourhood. The stability of these groupings is the same as in bulk liquid. The similar stability could be assumed also on solid-liquid interface. Both tested materials, namely silanized glass and PTFE, have identical surface energy and almost identical contact angles on these surfaces and were obtained for the alcohol-water mixtures in the whole concentration range as shown in Fig. 4. Therefore, we believe that alcohol and water molecules form stable aggregates on interfacial layers (liquid-air and solid-liquid). Although the composition of aggregates in bulk liquid and on the interface differs, this internal structure causes the higher contact angles when compared with pure liquids with the same surface tension.

5. Conclusions

An experimental study of the wetting behaviour of methanol, ethanol and *n*-propanol aqueous solutions on two similar hydrophobic surfaces in a full concentration range was conducted.

Alcohol-water mixtures exhibit notable aggregation of their molecules and this internal structure significantly influences the bulk liquid properties as viscosity or volume. On the basis of the experimental measurement of dynamic surface tension and dynamic liquid drop spreading we proved that in studied mixtures no dynamic adsorption of alcohol molecules occurs on liquid-air or liquid-solid interfaces in timescales greater than 10ms. Thus, the stable concentration both of water and alcohol molecules is assumed on the phase interfaces. It is possible to expect that the molecules located at the interface form aggregates with other molecules in their neighbourhood. The internal structure of such aggregates does not depend on the solid surface. This means that flat and homogenous surfaces which have similar surface energy should have similar wettability. To conclude, the complex internal structure of aqueous solutions of short chain alcohols, where the cross-association between water and alcohol molecules and following cluster formation are coming about, influences the surface properties of these solutions and the higher contact angles thus should be expected.

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Bubble adhesion onto the hydrophobic surface in solutions of non-ionic surface-active agents





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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Bubble adhesion onto a hydrophobic surface was captured using a high-speed camera.
- Three non-ionic surfactants differing in the structure were compared.
- The coherence between TPC line expansion, surface tension and wet-tability is studied.
- The suitability of non-ionic surfactants as flotation agents is discussed.

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ABSTRACT

Bubbles and drops are entities of enormous practical interest since their interfaces are encountered in numerous industrial processes. Froth flotation is just one of the examples in which bubble–particle attachment and especially fast bubble adhesion play a vital role. This work is focused on the experimental study of the three-phase contact (TPC) line expansion during the bubble adhesion onto the hydrophobic surface in solutions of three non-ionic surface-active agents (Terpineol, Triton X-100 and pentaethylene glycol monododecyl ether), which differ in their structure. The diameters of the TPC line together with bubble dynamic contact angles, dynamic surface tension, bubble rising velocity and dynamic drop contact angles were measured. It was confirmed that the bubble adhesion is fast in solutions of such surfactants whose hydrophobic and hydrophilic parts are small. On the other hand, surfactants with long and flexible hydrophobic tails exhibit more complex behaviour which usually leads to slower bubble adhesion. The molecule steric orientation in the proximity of the interface strongly influences the surfactant motion and thus the predictability of bubble attachment efficiency is low.

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1. Introduction

Over the past century, plastics have become an essential material being commonly used in a wide variety of applications due to their lightweight and excellent thermal and electrical insulation properties [1]. Plastics are used for medicinal purposes such as unblocking blood vessels or in prosthetics, in everyday products

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http://dx.doi.org/10.1016/j.colsurfa.2015.11.069 0927-7757/© 2016 Elsevier B.V. All rights reserved. including packaging for food and other goods, in the automotive industry, and in sports equipment and safety equipment like helmets or fire suits. The high demand for plastics means a high production rate with an estimated 57 million tonnes being produced in 2013 from the EU-27 alone, while simultaneously producing a high level of waste. By 2020, the EU-27 has set a target of having zero plastics dumped in landfills. This target was set because plastic products at the end of their life are too valuable to discard since they can be re-formed into their original state, utilised to generate heat and power from combined heat and power plants, or used to bolster plastic supplies.

Of the four stages in plastic recycling: collection, separation, processing/manufacturing and marketing, separation is considered to be the most important as only the highest quality resins can be used for preparing plastic or chemical products. Currently, methods such as gravitational separation, automatic sorting and electrostatic separation are used however each have their own advantages and disadvantages. The EU has invested in developing new methods for the separation of plastics after collection, including smart and green interfaces, to help reach its goal. This method utilises flotation to separate the plastics, an already proven efficient separation method in mineral processing where the attachment of bubbles increases the floatation of some materials while depressing others allowing separation to occur. During flotation, a stable froth has to be maintained above the flotation pulp in order to collect the floated valuable particles. Therefore the surface-active agents are added to the flotation liquid. Surfactants also adjust the required surface tension of the bulk liquid [2–4]. An important aspect of flotation is how the bubbles attach onto the particles and how the surfactants influence the expansion of the three-phase contact line between the bubble and the material for which currently little is known about [2].

Surfactants play an important role in interface science, commonly being used as wetting agents. Wetting agents are substrates that can enhance the ability of a solution to wet a solid surface allowing for easier spreading by lowering the surface tension of the liquid as well as the interfacial tension between the two liquids [5]. According to their structure, surfactants are amphipathic organic compounds that are composed of both a hydrophobic and hydrophilic section. Surfactants can be grouped into one of the following categories depending on the charge group on the head [6]: anionic, cationic, non-ionic and zwitterion.

In water, surfactants have two options to ensure each section interacts with its favoured environment. Firstly, it can arrange itself so that the hydrophobic head is above the water surface while the hydrophilic head is still submerged. Secondly, they can arrange into micelles, where the molecules form aggregates so that the head is exposed to water while the tail points towards the centre of the aggregate interacting with each other. The critical micelle concentration (CMC) is the concentration at which micelles form and any surfactant molecules that are subsequently added will join on to the micelles.

1.1. Bubble adhesion onto the hydrophobic surface

The bubble adhesion onto the hydrophobic particle and the stability of created unit determine the effectiveness of the whole separation process in flotation. It is commonly accepted that the bubble attachment consists of two terms: (1) the thinning of liquid film to a critical thickness where the rupture of the liquid film begins; and (2) the expansion of the three-phase contact line to form a stable wetting perimeter [7,8]. This perimeter is usually named as the three-phase contact line (TPC line). The rupture of the liquid film is a very quick process and thus its description is convoluted. Initially it was assumed that the rupture is connected with the density fluctuations and the TPC contact arises from a hole of a certain diameter in the intervening liquid film [2–10]. According to new findings the existence of nanobubbles attached to the solid surface is crucial [11–13]. After the formation of the TPC line its movement can be observed. Spontaneous movement occurs when the system is relaxing from nonequilibrium to an equilibrium state. In the literature, there are two approaches dealing with the kinetics of the TPC line based either on the hydrodynamic or molecular-kinetic theories. The hydrodynamic approach assumes mainly the viscous shear flow as a dissipative force [14,15] whereas the molecular-kinetic model follows the principles of surface chemistry. The theory is based on the statistical mechanics treatment of the transport processes of molecules and ions [16] and according to our findings the agreement with experimental data is excellent [17].

From the flotation perspective it is important that the bubble adhesion onto the solid surface is rapid, otherwise the flotation efficiency is low. In pure water, the stable perimeter of the TPC line is formed within a few milliseconds [18]. The surfactant presence may significantly affect the kinetics of this process. The TPC line dynamics could be influenced by the surfactant adhesion on solid–liquid, solid–gas and liquid–gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration [19]. This work is not focused on the explanation of the above mentioned phenomena although they will be discussed further. The aim is to compare three types of non-ionic surfactants differing in their structure and try to evaluate the bubble adhesion dynamics in solutions of these surfactants.

2. Experiments

2.1. Surfactants

The surfactants used in this study were α -Terpineol (here labelled as Terpineol, CAS No. 98-55-5), Triton X-100 (polyethylene glycol *tert*-octylphenyl ether, here labelled as Triton, CAS No. 9002-93-1) and pentaethylene glycol monododecyl ether (labelled as C₁₂E₅, CAS No. 3055-95-6). All surfactants were of high purity grade (\geq 98%) from Sigma–Aldrich and were used without further purification. Aqueous solutions of these surfactants with desired concentrations (see Table 1) were prepared by dilution with pure water (distilled, de-ionised and de-mineralised) at 25 °C.

2.2. Material

A silanized glass was used as a model hydrophobic surface. The silanization method is based on the covalent attachment of functional organosilanes to silica or glass. Silanes are believed to react with the exposed hydroxyl groups of silanols on the glass surface and, under optimal conditions, they form a uniform monolayer [20]. In our project the common type of silanized glass was used: the Silanization solution I was supplied by Sigma-Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The silanization method was applied according to recommendations from the literature [20]. The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water and dried. The slides were dipped into the silanization solution for 24 h, and then rinsed firstly with pure heptane then with acetone and ethanol in order to remove all organic residues, and finally they were dried. The silanized slides were stored in a dry place to avoid contact with air humidity. The surface homogeneity was tested using the AFM method. On clean glass, the maximum roughness reached a height of 60 nm (average 15 nm), and on silanized glass the maximum roughness reached a height of 160 nm (average 30 nm). The measurement was conducted within 1 week after preparation. Contact angles for pure water ranged from 103.1 to 104.3°.

2.3. Apparatus

The experimental measurements were performed in a special glass flotation cell (50 cm height, 8 cm width and 6 cm depth) using the freely rising method. Single bubbles were created by a bubble generator at the top of a thin capillary (inner diameter $10 \,\mu$ m, outer diameter $375 \,\mu$ m) and after detachment from the capillary the bubble rose through the liquid to the solid particle represented by silanized glass placed on a horizontal plane. The process of

Table 1

Characteristics of surfactants and their aqueous solutions used in the present study. Chemical formula, topological polar surface area according to PubChem[®], critical micelle concentration and used solution concentration.

Surfactant	Chemical formula and structure	Topological polar surface area (A ²)	CMC literature (mmol/l)	CMC experiment (mmol/l)	Measured concentrations (mmol/l)
	$C_{10}H_{18}O$				
2-(4-Methyl-1- cyclohex-3-enyl) propan-2-ol (α–Terpineol)		20.2	Not found	-	1.0, 2.0, 5.0
	$C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10)				
Polyethylene glycol <i>tert</i> -octylphenyl ether (Triton X-100)		103-110	0.22-0.24	0.21	0.1, 0.25, 0.5
	$C_{22}H_{46}O_{6}$				
Pentaethylene glycol monododecyl ether (C ₁₂ O ₅)	0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,	66.4	0.064-0.076	0.067	0.026, 0.045, 0.068, 0.134



Fig. 1. Sequences of photos illustrating a course and outcome of the bubble collision and adhesion onto the solid surface. C12E5 solution (0.045 mmol/l), db = 0.696 mm.

bubble–particle interaction, i.e. the bubble motion before the collision with the solid particle and during the adhesion was recorded using high-speed digital camera (2 000 fps, resolution of 1280×256 pixels) Redlake Motion Scope M2 with the macroobjective Navitar. Images were evaluated using the image analysis software NIS-Elements and MatLab software, calculations were performed using the MatLab software. Between 3 and 5 series (of desired bubble size) were generated for each surfactant concentration and each series consists of 10 measurements. The resulting diameters of the TPC line ($d_{\rm TPC}$) and bubble contact angles ($\theta_{\rm b}$) were calculated as the average of at least five measurements.

2.4. Experimental methods

The equilibrium surface tension was measured by a tenziometer Lauda TD1 using the Pt/Ir ring tenziometer method (du Nouy's method). The accuracy of the surface tension measurements by this tenziometer was 0.15 mN/m. In all cases, more than 10 successive measurements were performed. The standard deviation did not exceed 0.2 mN/m. This method was used for the CMC determination. Dynamic surface tension was determined by the maximum bubble pressure method using the Krűss BP100 tenziometer. The surface age ranged from 10 ms to 50 s. All experiments were done at 25 °C \pm 0.2 °C. The drop contact angles (θ_d) were measured too. A Cohu monochrome CCD camera with a 752 × 548 pixel resolution was used to capture the drop images with a frame velocity of 15 fps. At least nine drops (V = 15 µl) on three slides were taken for each surfactant solution. NIS-Elements software was utilized for the image processing where the drop profile together with drop height, length and contact angles were analysed. The liquid drop was formed by pumping the liquid using a motor-driven syringe placed in an adjustable holder. Measurement with pure water was done before each set of measurements in order to ensure the stable wettability of the solid surface.

3. Results

3.1. Description of the experiment

As a typical example, Fig. 1 shows data obtained within one experimental set. The adhesion of a bubble with diameter 0.696 mm in 0.045 mmol/l solution of $C_{12}E_5$ is given here. The bubble approched the solid surface (A) and after the collision one rebound was observed (B and C). Then the bubble remained still for 0.2 s(D). The time when the rupture of thin liquid film occurs was set as a zero time (E). After this moment a rapid TPC line expansion was observed (F–H). After 0.1 s the expansion slowed (I). The capturing was interrupted after 0.68 s (J). At this time the bubble



Fig. 2. The calculated diameters of the TPC line and contact angles for bubble with $d_b = 0.696$ mm. Example of bubble adhesion in C₁₂E₅ solution (0.045 mmol/l).

shape was stable and the diameter of the TPC line together with contact angles did not change for more then 0.1 s. The calculated diameters of the TPC line and contact angles are depicted in Fig. 2. The non-zero diameters of TPC line and contact angles during the period before the liquid film rupture have no physical meaning and these values result from the image analysis (see detail D in Fig. 1), where the software is not able to differentiate the thin liquid film between the bubble and solid surface. The dynamic contact angles $\theta_{\rm b}$ were calculated using the ADSA method which exploits the best fit of point coordinates around the bubble [21]. A close relationship between the TPC line diameter and dynamic contact angle is evident and follows theoretical assumptions published previously by Blake and Haynes [22].

3.2. Bubble rising velocity

When surfactants are present in the fluid, they absorb at the interface of a rising bubble and accumulate in the bubble rear section. In this case the shear stress is higher and consequently the bubble drag increase, with an immobilization of the gas–liquid interface. This is manifested by an increase of the drag coefficient C_d . Thus by using the measurement of bubble terminal velocity we can characterize the mobility of bubble surface.

The terminal bubble velocity $U_{\rm b}$ could be calculated using the drag coefficient which is a function of bubble Reynolds number. The relation for the drag of solid spherical particles is also applicable for bubbles with surfaces immobilized by surfactants [23]. All experimental terminal bubble velocities were consistent with the theoretical values. Therefore we could consider the immobility of bubble surface. It means that at least the rear part of the bubble surface was covered by surfactants. The only exception was the most diluted solution of $C_{12}E_5$, where the velocity for $d_b > 0.7$ mm was increased by 15%. This fact indicates the lower coverage by surfactants.

3.3. Dynamic surface tension

Fig. 3 illustrates the dependence of dynamic surface tension for solutions of Terpineol, Triton and $C_{12}O_5$ as functions of the surface age. This quantity represents the time needed to create a new bubble of desired size. For pure liquids the surface tension does not depend on the bubble surface age and we obtain the same value regardless of the method of measurement. For pure water, the surface tension at 25 °C is 72.1 mN/m. In solutions of surfactants, the surface tension changes over time. A freshly formed interface of a surfactant solution has a surface tension very close to that of a solvent. Over a period of time, surface tension will decay to its



Fig. 3. Dynamic surface tension of measured surfactant solutions.

equilibrium value and this period of time can range from milliseconds to days depending on the surfactant type and concentration. For concentrations below the CMC, there are two main models for monomer transport and adsorption: diffusion controlled model and mixed kinetic-diffusion model. Above the CMC, the micelles present in the solution have a certain lifetime for break-up. If the micelles are stable entities with long lifetimes, the molecules in the micelles may not be available for adsorption. In effect, the concentration of molecules diffusing to the interface will be equal to the CMC, regardless of the bulk concentration of surfactant [24].

Terpineol belongs to simple surfactants and is considered to be one of the most important flotation agents. We did not find any information about the micelle formation and critical micelle concentration. Nevertheless it is apparent from Fig. 3A that Terpineol exhibits the typical decrease of surface tension over time. For higher concentrations (5 mmol/l) the decrease is evident even after 10 milliseconds, so the timescale of adsorption from the subsurface to the interface is very fast. Thus the simple model of adsorption process should be considered.

Triton is a more complex molecule. As shown in Fig. 3B, for surfactant concentration both below and above CMC the surface tension decreases to its equilibrium value. The initial adsorption occurs after 10 ms and the process reaches the equilibrium roughly after 50 s. Similar values were obtained by Fainerman [25]. Due to the time lag in the beginning of adsorption the mixed kinetic-diffusion model is to be expected. There is an adsorption barrier preventing the monomer from adsorbing. This barrier may be due to increased surface pressure, less 'vacant sites' available for adsorption or there may also be steric restraints on the molecule in the proximity of the interface, and it may have to be in the correct orientation to adsorb [24].

The slowest adsorption occurs in the case of $C_{12}O_5$. As follows from Fig. 3C, the initial adsorption occurs after 100 ms and the equilibrium was not reached even after 50 s. The molecule of $C_{12}O_5$ is long and flexible. In such cases it could be expected, that the previously adsorbed molecules even prevent other molecules from adsorbing. It could be concluded from the measured data that the quickest adsorption could be expected for Terpineol solutions.

3.4. Liquid drop spreading

The dependence of the contact angle (sessile drop on silanized glass) for solutions of Terpineol, Triton and $C_{12}O_5$ as functions of time is illustrated in Fig. 4. The contact angle for pure water remains stable whereas for surfactant solutions we can observe typical spreading behaviour [26]. The authors believe that the measured values are not strongly influenced by the evaporation effect and thus no correction was done.

The studied solutions of Terpineol exhibit a lower decrease in surface tension when compared with pure water. Thus the contact angles are comparatively high. Solutions of Triton and $C_{12}E_5$ have significantly lower surface tension ranging from 50 to 30 mN/m and the measured contact angles are also lower. The complete spreading was not observed for any studied solutions. From these measurements we are not able to evaluate the influence of surfactant adsorption onto the solid–liquid interface. Nevertheless it could be assumed that the adsorption on liquid-air interface is dominant for the bubble/drop wetting dynamics when compared with the influence of surfactant adhesion onto the liquid–solid interface.

3.5. Bubble dynamic contact angles

Although the descriptions of both drop and bubble shapes are based on the same theoretical background, the literature concerned with the description of bubble shape is scarce [21]. Moreover when images of a sessile drop and a sessile bubble are compared, the quality of the bubble image is usually lower. It is due to the light reflection at both the solid–liquid (vessel) and gas–liquid (bubble) interfaces and usually also due the lower pixel resolution of highspeed cameras. In our measurements we believe that the accuracy of the contact angle determination is $\pm 3^{\circ}$.

For small drops of pure liquids the contact angle does not change with changing drop size [27]. For example it is valid for water below the drop radius of 2.7 mm. Otherwise we should consider both capillary and gravity forces acting on the sessile drop. The capillary length κ characterizes the mutual relation between the gravitational/buoyancy acceleration and the surface force due to the liquid surface tension. For bubbles with diameters below 1 mm we can almost neglect the influence of buoyancy because $\kappa \approx 8.5$ cm. Thus in pure water we should expect the independence of equilibrium bubble contact angle on bubble size. This was proven as demonstrated in Fig. 5A.



Fig. 4. Contact angles of surfactant solutions droplets on silanized glass.

In the case of surfactant solutions we should consider both the preferential adsorption of surfactant molecules on the phase interfaces and motion dynamics of surfactant molecules towards and on the bubble surface. Consequently the bubble equilibrium contact angle may vary with increasing bubble diameter. This phenomenon is illustrated in Fig. 5B. Here the contact angles for four bubble diameters in 0.045 mmol/l solution of $C_{12}E_5$ are given. The equilibrium contact angles range from 30.9 to 48.7° . This difference is the biggest one; we observed much smaller changes in the dependence of contact angle on bubble size also for solutions of Triton. These results will be discussed in the next chapter. It should be noted that the angle oscillations (clearly visible for $d_b = 0.70$ mm) were caused by the variations in light intensity due to the alternating current.



Fig. 5. Dynamic bubble contact angles in water and $C_{12}E_5$ solution (0.045 mmol/l).

3.6. The three-phase contact line expansion

The stability and velocity of bubble attachment determines the effectiveness of the whole separation process in flotation. Thus both fast adhesion process and high contact angles are required. Unfortunately the accuracy of contact angle measurement is relatively low and therefore primarily the three-phase contact line diameters d_{TPC} were measured and discussed. Here, the close relationship between time course of the TPC line diameter and dynamic contact angle is considered [22]. In order to highlight the influence of surfactant adsorption on bubble shape we evaluate the ratio d_{TPC}/d_b . For systems where the bubble size does not influence the contact angle the ratio remains constant. On the other hand, in case of surfactants with a complex adsorption dynamics we assume the changing ratio.

The results are illustrated in Fig. 6. For comparison, data obtained for pure water are also given here [17]. For pure water (detail A), similarly as is the case with dynamic bubble contact angles, the independence of ratio d_{TPC}/d_b on bubble size was observed. The experimental value 1.24 matches with the theoretical assumption. The theoretical ratio calculated for an absolutely spherical bubble and contact angle $\theta_b = 90^\circ$ is 1.26. The stable bubble position (expressed as 95% of equilibrium d_{TPC}) was achieved in 20 ms. The obtained bubble dynamics meets the requirements of a fast dynamics and stable bubble attachment but in real industrial applications we use solutions of flotation agents.

Data for Terpineol solutions are given in detail B. For all concentrations, the adsorption process is very fast and the stable bubble position was achieved within 30 ms. This time is considered to be sufficient even for industrial processes performed in mixed batches. Also the bubble attachment is stable since the ratio d_{TPC}/d_b is 1.0 and 1.1 for concentrations 5 and 2 mmol/l, respectively. The equilibrium contact angles were 70° (conc. 5 mmol/l) and 82° (conc. 1,

2 mmol/l) while the dependence of contact angle on bubble size was negligible. These high contact angles also ensure the stable bubble position for high concentrations where the surface tension is close to 50 mN/m. According to the dynamic surface tension measurements, the timescale of adsorption from the bulk liquid to the interface is very fast. To conclude all known information about Terpineol we can summarize that terpineol molecules are small, their transport from the bulk to the interface is fast and the bubble attachment is stable. In terms of flotation terpineol seems to be an excellent flotation agent.

When comparing Terpineol and Triton molecules we can see that the hydrophobic part containing the benzene ring is similar for both surfactants. On the other hand, the hydrophilic part differs and the Triton's "head" is longer because it contains 9-10 oxygen atoms. Also its topological polar surface area is about 5 times larger. Therefore it can be assumed that the bubble adsorption is much slower. This assumption was fulfilled and the results are illustrated in Fig. 6C. The stable bubble position which is close to the equilibrium was achieved for up to 300 ms. Almost equal results were obtained for solutions with concentrations both bellow and above CMC. The ratio d_{TPC}/d_b ranged from 0.7 to 0.8. The ratio value below 0.9 indicates unstable bubble attachment with low contact angles. For all Triton's solution the equilibrium contact angles ranged from 48 to 54° and the dependence of contact angle on bubble size was again insignificant. Hence from a flotation point of view Triton seems to be an unsuitable agent. Nevertheless the bubble adsorption dynamics is predictable. It could be concluded from the dynamic surface tension measurement that within 1s the bubble surface is covered by a sufficient amount of surfactant molecules. The total bubble life time in our experiment is much longer because it consists of (i) the time of bubble formation on a capillary tip, (ii) the time of the bubble rising to the solid surface and (iii) the time delay due to the liquid film thickening before the TPC line expansion. During the rising movement the surfactant molecules are located in the rear section and form a stagnant cap [28]. The time delay, when the liquid film thinning occurs, takes a few seconds and due to the concentration gradient the surfactant molecules could distribute over the entire bubble surface. We think that the surfactant molecules which are present in the close vicinity of the three-phase interface prevent the fast TPC line expansion.

The results obtained for C₁₂E₅ solutions are given in Fig. 6D. It is clearly visible that d_{TPC} is strongly influenced by both the surfactant concentration and bubble size. The ratio d_{TPC}/d_b increased with increasing bubble size as in the case of bubble contact angles (see Fig. 5B). Only for the concentration 0.068 mmol/l, which is equal to the CMC concentration, the influence of bubble diameter was negligible. For large bubbles $(d_b = 0.72 \text{ mm})$ and low concentration (0.026 mmol/l) the stable bubble position was achieved within 20 ms. This period is similar to pure water or Terpineol solutions. On the other hand, for high concentrations the bubble adsorption was achieved for up to 400 ms and $d_{TPC}/d_b \approx 0.5$. The bubble adsorption is slower than for Triton solutions. Thus it is clear from these mentioned data that any prediction of bubble adhesion dynamics or flotation efficiency is very problematic. In terms of flotation C₁₂E₅ seems as absolutely unsuitable flotation agent. But still the question remains, how to explain such behaviour.

In case of large or else complex molecules, an adsorption barrier preventing the monomer from adsorbing should be expected [24]. This barrier comes into existence in dilute solutions, then rises with increasing concentration and again changes close to the CMC concentration. The existence of such a barrier is often connected with some steric restraints on the molecule in the proximity of the interface, because the molecules should be in the correct orientation. Unsuitable orientation could cause the molecule to diffuse back into the bulk rather than adsorbing. Moreover Rutland and Senden [29] showed that polyoxyethy1ene based surfactant could create small



Fig. 6. The ratio d_{TPC}/d_b for bubble adhesion in water and surfactant solutions.

aggregates and so the spatial orientation of molecules on the interface changes with increasing surfactant concentration. We assume that for large bubbles and low concentration the attachment of $C_{12}E_5$ molecules in the stagnant cap is very stable. The molecules could not overcome the concentration gradient and thus they are not present in the vicinity of future TPC lines. For smaller bubbles the overcoming distance is shorter and the molecules hinder the TPC line expansion more easily. The extremely slow transport of $C_{12}E_5$ molecules was proven using the dynamic surface tension measurement. Anyhow, the behaviour of $C_{12}E_5$ is highly non trivial and should be studied in more detail in order to explain the dependence of bubble contact angle on bubble size.

4. Conclusion

In the present work we have analysed the influence of non-ionic surfactants on dynamics of bubble adhesion onto the hydrophobic surface. Here, the enormous influence of surfactant size and structure was observed. The bubble adhesion is fast in solutions of such surfactants, whose hydrophobic and hydrophilic parts are small. Due to the immediate transport of molecules onto the liquid-gas interface the decrease of surface tension is fast and also the small molecules do not significantly hinder the TPC line expansion. Terpineol seems like a typical representative of such a substance. The bubble attachment is stable even in solutions with higher concentration (with lower surface tension) and therefore Terpineol can be recommended as a suitable flotation agent.

Surfactants with long and flexible hydrophobic tails exhibit slower and more complex behaviours. In general we can say that the bubble adhesion is very slow in solutions with surfactant concentration close to or above CMC. Simultaneously the bubble interception is unstable. At lower concentrations, both the surfactant structure and bubble size play an important role. We assume the existence of adsorption barriers close to the interfaces which influences the surfactant motion. Molecules of pentaethylene glycol monododecyl ether are very long and could create certain small aggregates captured on the phase interface. The transport of such molecules is very low and thus, surprisingly, their influence on the velocity of TPC line expansion could be very low. Similar phenomena were not observed for Triton solutions. The explanation of the observed complex behaviour is far more speculative; but it is certain that non-ionic surfactants with long hydrophobic chains are unsuitable as flotation agents.

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Bubble adhesion on hydrophobic surfaces in solutions of pure and technical grade ionic surfactants



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Bubble adhesion onto a hydrophobic surface was captured using a high-speed camera.
- Two typical ionic surfactants differing in purity were compared.
- The coherence between TPC line expansion, surface tension and wet-tability is studied.
- The significant influence of contaminants even in trace concentration is discussed.



A R T I C L E I N F O

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ABSTRACT

The attachment of bubbles onto a collecting surface plays a critical role in many industrial processes. Here, the bubble behaviour is crucially influenced by the presence of surface active agents, where the ionic surfactants are the most common agents. The ionic surfactants very often contain contaminants which, even in trace amounts, could unexpectedly influence the bubble adhesion. This work is focused on an experimental study of bubble adhesion onto the hydrophobic surface in solutions of two ionic surface-active agents (DTAB and SDS) of pure and technical grade purity. The diameters of the three-phase contact line together with bubble dynamic contact angles, dynamic surface tension and dynamic drop contact angles are measured. It was observed that the contaminants decrease the ability of bubbles to attach to solid surfaces when compared with the mono-surfactant solution. The influence of contaminants is crucial below the critical micelle concentration of the main surfactant and it may even happen that the capture of bubbles is avoided.

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1. Introduction

lonic surfactants are the largest group of surfactants used today with more than 75% of total worldwide consumption. Within the anionic group there are sulphate esters, sulfonic acid salts, carboxy-

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http://dx.doi.org/10.1016/j.colsurfa.2017.03.024 0927-7757/© 2017 Elsevier B.V. All rights reserved. late soaps and detergents and phosphoric acid esters. The sulphate ester family is one of the most significant due to the sodium dodecyl sulphate (SDS); the most widely studied and used surfactant. Cationic surfactants are important in cosmetics as antiseptic agents, as fungicides, germicides, fabric softeners and hair conditioners. The sources of hydrophobic groups are mostly natural fatty acids or derivatives from petrochemical compounds; in all cases they contain nitrogen. One of the most studied cationic surfactants is dodecyltrimethylammonium bromide (DTAB). The ionic surfactants used both in industrial applications and in scientific studies, as a rule, contain some admixtures of non-ionic surfactants or other contaminants. The principal organic contaminants are homologous alkyl sulphates, n-alcohols and carboxylic acids. It is extremely difficult to prepare SDS that is sufficiently pure for surface chemistry [1]. Dodecanol is the most important contaminant and is one of the hardest to remove [2-5]. Even at impurity levels below 0.1%, dodecanol reduces the surface tension and leads to the well-known minimum below the critical micelle concentration (CMC). Dodecanol also significantly influences the surfactant adsorption on the solid-liquid interface [1,6]. The presence of dodecanol in SDS solutions has a dramatic effect not only on the surface properties, but also on shear viscosity and foam stability [1,7]. In contrast to the air-water interface, traces of dodecanol have little effect on the oilwater interface because dodecanol is highly soluble in the oil phase [8]. The coadsorption is most often studied on liquid-air interface [2-4,9] using the dynamic surface tension measurements and on hydrophobic surface by sum-frequency spectroscopy [1].

Flotation is a separation method based on the ability of some solids to remain attached to the gas-liquid interface. The attachment of bubbles onto a collecting surface plays a critical role in flotation, which is utilized for the separation of mineral ores, coal or plastic materials. An important aspect of flotation is how the bubbles attach onto the particles and how the surfactants influence the expansion of the three-phase contact line between the bubble and the material for which little is currently known about [10,11]. The bubble adhesion onto the hydrophobic particle and the stability of the created unit determine the effectiveness of bubble-particle interactions. The bubble attachment consists of two terms: (1) the thinning of liquid film to a critical thickness where rupture of the liquid film begins; and (2) the expansion of the three-phase contact line to form a stable wetting perimeter [11,12]. This perimeter is usually known as the three-phase contact line (TPC line). After the formation of the TPC line its movement can be observed. Spontaneous movement occurs when the system is changing from nonequilibrium to an equilibrium state. The literature mentions two main approaches when dealing with the kinetics of the TPC line based either on the hydrodynamic [13,14] or molecular-kinetic theories [15,16]. In pure water, the stable perimeter of the TPC line is formed within a few milliseconds [17] but the presence of surfactants may significantly affect the kinetics of this process [18–21]. The TPC line dynamics is influenced by the surfactant adhesion on solid-liquid, solid-gas and liquid-gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration [22]. In our previous study, three non-ionic surfactants, differing in size and structure, were studied [23]. According to our conclusions, the bubble adhesion is fast in solutions of such surfactants, whose hydrophobic and hydrophilic parts are small (Terpineol). Due to the fast transport of such molecules onto the liquid-gas interface, the decrease of surface tension is fast and the small molecules do not significantly hinder the TPC line expansion. On the other hand, greater or longer molecules of surfactants (Triton X-100, pentaethylene glycol monododecyl ether) move slower and the velocity of bubble adhesion decreases significantly. Long and flexible molecules could create certain small aggregates captured on the phase interface or we can observe the existence of adsorption barriers close

to the interfaces influencing the surfactant motion. The dynamics of TPC expansion is thus complicated and the prediction of bubble behaviour is almost impossible. The ionic surfactants differ from the non-ionic's by the presence of positively (cationic) or negatively (anionic) charged groups on the hydrophilic part of the molecule. Their impact on bubble-particle interactions is extremely influenced by the presence of contaminants. The coadsorption leads to a significant decrease of the interfacial tensions which influences the final contact angle. Thereby the bubble attachment efficiency lowers, which has a significant impact on the entire flotation process. The flotation attachment efficiency is generally formulated for moving spherical particles and bubbles and it is defined by the ratio of the number of captured bubbles onto the particle surface to the number of colliding bubbles.

The paper presents results on the influence of different ionic surfactants on the kinetics of the three phase contact (TPC) line formation on a hydrophobic solid surface. Experiments were carried out in pure and technical grade solutions of cationic *n*-dodecyltrimethyl-ammonium bromide (DTAB) and anionic sodium dodecyl sulphate (SDS). The influence of contaminants on bubble attachment, bubble adhesion dynamics and velocity of TPC enlargement is described and discussed.

2. Experiment

2.1. Surfactants

Surfactants SDS and DTAB were purchased from Sigma-Aldrich Chemical Company. They were used as received. Pure SDS with declared purity \geq 99%, which is designated for ion pair chromatography (catalogue number 71726), will be denoted as HP-SDS (high purity). Technical-grade SDS, with declared purity \geq 98.5% (catalogue number L4509), will be denoted as LP-SDS (low purity). Pure DTAB, which is marked as suitable for ion pair chromatography (catalogue number 44239, purity \geq 98.5%) will be denoted as HP-DTAB (high purity). Technical-grade DTAB, with declared purity \geq 98% (catalogue number D8638), will be denoted as LP-DTAB (low purity). Aqueous solutions of these surfactants with desired concentrations (see Table 1) were prepared by dilution with pure water (distilled, de-ionised and de-mineralised using the WATREX ULTRAPURE system) at room temperature.

2.2. Material

A silanized glass was used as a model hydrophobic surface. The silanization method is based on the covalent attachment of functional organosilanes to silica or glass. Silanes are believed to react with the exposed hydroxyl groups of silanols on the glass surface and, under optimal conditions, they form a uniform monolayer. In our project the common type of silanized glass was used: the Silanization solution I was supplied by Sigma-Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water and dried. The slides were dipped into the silanization solution for 24 h then rinsed firstly with pure heptane, then with acetone and ethanol in order to remove all organic residues, and finally they were dried [23]. The silanized slides were stored in a desiccator to avoid contact with air humidity. The measurement was conducted within 1 week after preparation. Contact angles for pure water ranged from 103.1 to 104.3°.

2.3. Surface tension measurements

The static surface tension was measured at 25 °C by the stalagmometric method, using a laboratory-made apparatus [24].

Table 1

Characteristics of surfactants and their aqueous solutions used in the present study. Chemical formula, critical micelle concentration and used solution concentration.

surfactant	chemical formula	CMC literature (mmol/l)	CMC experiment (mmol/l)	concentrations (mmol/l)
sodium dodecyl sulphate (SDS)	C ₁₂ H ₂₅ SO ₄ ·Na	8.3	8.9	5.2, 8.3 and 17.3
dodecyltrimethylammonium bromide (DTAB)	C ₁₅ H ₃₄ BrN	15.6	15.8	6.5, 9.7, 13.0 and 16.2

Dynamic surface tensions were measured at 25 °C by the maximum bubble pressure method, using the BP100 tenziometer from Krűss.

2.4. Drop contact angles (θd)

A Cohu monochrome CCD camera with a 752×548 pixel resolution was used to capture the drop images with a frame velocity of 15 fps. At least nine drops (V = 15 μ l, $d_d \approx 5$ mm) on three slides were taken for each surfactant solution. NIS-Elements software was used for the image processing where the drop profile together with drop height, length and contact angles were measured. The liquid drop was formed by pumping the liquid using a motor-driven syringe placed in an adjustable holder. The measured contact angles therefore correspond to advancing angles. Measurement with pure water was done before each set of measurements in order to ensure the stable wettability of the solid surface. The accuracy of the contact angle measurement was $\pm 1^{\circ}$.

2.5. Bubble adhesion

The experimental measurements were performed in a special glass flotation cell (50 cm height, 8 cm width and 6 cm depth) using the freely rising method. Single bubbles were created by a bubble generator at the top of a thin capillary (inner diameter 10 μ m, outer diameter 375 μ m) and after detachment from the capillary the bubble rose through the liquid to the solid particle represented by silanized glass placed on a horizontal plane. The process of bubble-particle interaction, i.e. the bubble motion before the collision with the solid particle and during the adhesion, was recorded using a high-speed digital camera Redlake Motion Scope M2 (2 000 fps, resolution of 1280 × 256 pixels) or Photron FastCam SA1.1. (5600 and 16000fps, resolution of 1024 × 1024 pixels) with the macroobjective Navitar.

2.6. Image analysis

Images were evaluated using the image analysis software NIS-Elements and MatLab software, calculations were performed using the MatLab software. Between 3 and 5 series (of desired bubble size) were generated for each surfactant concentration and each series consisted of 10 measurements. The resulting diameters of the TPC line (d_{TPC}) and bubble contact angles (θ_{b}) were calculated as the average of at least five measurements. In classical terminology, where contact angles are conventionally measured through liquid, the bubble contact angle would be described as the receding angle. Fig. 1 shows data obtained within one experimental set. The adhesion of a bubble with diameter 0.733 mm in 9.7 mmol/l solution of HP-DTAB is given here. The bubble approached the solid surface (A) and then the bubble remained still for 0.4 s (B). The time when the rupture of thin liquid film occurs was set as a zero time (C). After this moment a rapid TPC line expansion was observed (D). After 0.1 s the expansion slowed (E). The capturing was interrupted after 0.5 s (F). At this time the bubble shape was stable and the diameter of the TPC line together with contact angles did not change for more than 0.1 s. The position of solid surface and bubble contour are illustrated in the detail G. The accuracy of the measurements was

 $\pm 6\,\mu m$ (which corresponds to 2 pixels) and $\pm 2^\circ$ (bubble contact angle), respectively.

3. Results and discussion

3.1. Static and dynamic surface tension

In Figs. 2 and 3, the surface tensions γ_{LG} of aqueous solutions of SDS and DTAB, respectively, are plotted versus the surfactant molar concentration. The simple stalagmometric method was used for the CMC determination. The low-purity compounds were used for this purpose in order to determine if the prepared solutions have concentrations below, around and above CMC. From the data in Table 1 it is clear that the experimentally determined values of CMC do not differ significantly from data recommended in the literature [25,26]. The obtained values are supplemented with experimental data obtained using the maximum bubble pressure method (bubble surface age 10 s) both for HP and LP compounds. For comparison, the graph includes recommended data on surface tension which were measured by Mysels [4] and Stubenrauch [27].

Figs. 4 and 5 illustrate the dependence of dynamic surface tension for solutions of HP and LP SDS and DTAB as a function of the surface age. This quantity represents the time needed to create a new bubble of desired size. For pure liquids the surface tension does not depend on the bubble surface age and we obtain the same value regardless of the method of measurement. For pure water, the surface tension at 25 °C is 72.1 mN/m. In solutions of surfactants, the surface tension changes over time. A freshly formed interface of a surfactant solution has a surface tension very close to that of a solvent. Over a period of time, surface tension decays to its equilibrium value and this period of time can range from milliseconds to days depending on the surfactant type and concentration. Both SDS and DTAB are small molecules and their diffusion from bulk liquid to the water-air interface is quick. Therefore, even after 10 milliseconds we observed a substantial decrease of surface tension. The surface tension is similar for HP and LP surfactants for the bubble surface age up to 1 s. For bubbles older than 1 s we observed significant differences between HP and LP surfactants. For pure SDS the surface tension slowly decreases and reaches the equilibrium value after 10 s. DTAB also has a similar pattern. Here, an additional small decrease was detected after 30 s. According to Fainerman [9], for long periods one should consider the aging of the solution and gradual hydrolysis. But such long bubble ages are not important in most industrial applications. Low purity surfactants show an important decrease of surface tension for bubble surface age over 1 s. At this time the presence of contaminants becomes crucial. For SDS at a concentration of 8.3 mmol/l, which is close to CMC, the surface tension lowers to 23 mN/m, which is 15 mN/m less than for the HP. For concentrations close to CMC, the resultant surface tension is lower than the tension for solutions above CMC. This behaviour is explained by the preferred adsorption of contaminants on the interphase. Mysels [4] emphasized that thermodynamically meaningful equilibrium tension values can be obtained at intermediate times; after adsorption of the main surfactant component is almost complete and before adsorption of the highly surface active contaminants become significant. This argument is supported by the prediction based on a binary diffusion-controlled adsorption model



Fig. 1. Sequences of photos illustrating a course and outcome of the bubble (d_b = 0.73 mm) adhesion onto the solid surface in HP-DTAB solution (9.7 mmol/l).



Fig. 2. Experimental surface tension vs. concentration for SDS solutions.



Fig. 3. Experimental surface tension vs. concentration for DTAB solutions.

[28], which considers a system containing 1% of an impurity that is 100 times more surface active than the main component. The surface molar concentration of dodecanol is multiple times higher than in the bulk. According to Ward[1], the amount of dodecanol in the monolayer reaches a maximum below the CMC. Kralchevsky [5] states that even a trace amount of dodecanol in bulk (0.053 mol%) could increase its surface molar fraction up to 42%. The preferential adsorption of dodecanol also explains the differences of measured surface tension in Figs. 2 and 3.

Above the CMC, the micelles that are present in the solution have a certain lifetime for break-up. If the micelles are stable entities with long lifetimes, the molecules in the micelles may not be available for adsorption. Consequently, the concentration of molecules diffusing to the interface will be equal to the CMC, regardless of the bulk concentration of the surfactant. When contaminants are present in the solution, the CMC is lower. The increase in surface tension of the unpurified surfactant above CMC could be caused by the solubilisation of dodecanol in SDS micelles and the consequent desorption of dodecanol from the bubble surface.

To conclude this part, the significant effect of contaminants on surface tension was confirmed. This effect is dominant for concentrations bellow CMC.



Fig. 4. Dynamic surface tension plotted as function of bubble surface age. High purity (HP) and low-purity (LP) SDS solutions at different concentrations.



Fig. 5. Dynamic surface tension plotted as function of bubble surface age. High purity (HP) and low-purity (LP) DTAB solutions at different concentrations.



Fig. 6. Contact angles of surfactant solutions droplets on silanized glass. High purity (HP) and low-purity (LP) SDS solutions at different concentrations.



Fig. 7. Contact angles of surfactant solutions droplets on silanized glass. High purity (HP) and low-purity (LP) DTAB solutions at different concentrations.

3.2. Dynamic liquid drop spreading

The dependence of the advancing contact angle (sessile drop on silanized glass) for solutions of LP-DTAB and LP-SDS as a function of time is illustrated in Figs. 6 and 7. The contact angle for pure water remains stable whereas for surfactant solutions we observed a typical spreading behaviour. The authors believe that the measured values are not strongly influenced by the evaporation effect and thus no correction was done. The complete spreading was not observed for any studied solutions, although for SDS we observed very low contact angles (28° for concentration 8.3 mmol/l). The largest decline occurred in the first 50 s. Both for DTAB and SDS, the solutions with concentration around CMC show the lowest contact angles and therefore the highest wettability. This result coheres with the lowest surface tension and also with the presumed adhesion of surfactant molecules onto the solid-liquid interface [6]. Co-adsorption of dodecanol and SDS on a hydrophobic surface was studied in detail by Ward [1]. According to this study, the monolayer at the solid-water interface is denser and much richer in dodecanol than the corresponding monolayer at the surface of the water. Although the drop and bubble contact angles differ significantly, the study of drop spreading could indicate if some contaminants are present in the solution. In that case we do not observe the linear relationship between the drop contact angle and the surfactant concentration.

3.3. Captive bubble

In pure water for a bubble diameter smaller than 1 mm, the equilibrium bubble contact angle is independent of bubble size because the buoyancy could be neglected [23]. With increasing bubble size the bubble shape changes from spherical to buoyancy-deformed but the contact angle remains the same. In the case of surfactant solutions we should consider the influence of preferential adsorption of surfactant molecules on both phase interfaces. For all solutions, bubbles with diameters ranging from 0.6 to 0.9 mm were studied and the independence of the contact angle on bubble size was proven. Small differences, which amounted to a maximum of 2°, were probably caused by the measurement inaccuracy. In all experiments, the dynamic bubble contact angle increases from the zero value to the equilibrium contact angle θ_{eq} and the form of its time dependence is similar to that of the diameter of the TPC line. The final equilibrium contact angles are listed in Figs. 8 and 9.

When the equilibrium drop and bubble contact angles for identical solutions (Figs. 6-9) are compared we notice certain deviations. They can be explained by two reasons. Firstly we should consider the contact angle hysteresis because the advancing contact angles were measured for drops whilst receding contact angles were obtained for bubbles. According to Drelich [29], the increasing roughness and heterogeneity of the solid surface causes differences between the measured receding contact angles when determined with different methods, sessile-drop or captive-bubble. Similar discrepancies between the two experimental techniques, but to a lesser extent, are observed for advancing contact angles. The capillary length characterizes the mutual relation between the gravitational (or buoyancy) acceleration and the surface force due to the liquid surface tension. For water and our solutions at standard temperature and pressure, capillary length is approximately 2 mm. A capillary surface whose largest dimension is much smaller than the capillary length will take the shape of a spherical cap, which is the solution of the Young-Laplace equation when buoyancy is completely neglected. Thus for bubbles with diameters from 0.5 to 0.9 mm, the influence of surface forces is dominant over the influence of buoyancy. In cases where drops have a diameter of around 3-4 mm, the influence of gravity is much more significant and drops are less spherical. Therefore, a certain error could occur during the image data processing. The second reason is the different range of surfactant adhesion onto the liquid-solid and liquid-gas interfaces which is discussed below.

3.4. Three-phase contact line expansion

The bubble attachment determines the effectiveness of the bubble-particle interaction process. In our model situation, where a bubble attaches to the horizontal solid surface, the bubble adhesion efficiency could be expressed by the equilibrium contact angle. The efficiency is zero for the zero contact angle and increases to 1 with increasing contact angle. For a stable bubble position, fast adhesion velocity and high contact angles are needed. Here, the close relationship between the time course of the TPC line diameter and the dynamic contact angle is considered [16]. In order to highlight the influence of surfactant adsorption we evaluate the ratio d_{TPC}/d_b . For systems where the bubble size does not influence the contact angle, the ratio remains constant. The theoretical ratio calculated for an absolutely spherical bubble and contact angle 90° is 1.26. The experimental value 1.32, achieved for pure water, matches with this



Fig. 8. The ratio d_{TPC}/d_b for bubble adhesion in SDS solutions.



Fig. 9. The ratio d_{TPC}/d_b for bubble adhesion in DTAB solutions.



Fig. 10. The velocity of three-phase contact line in DTAB solutions.

theoretical assumption and reflects the facts that the real bubble is axisymmetric and the contact angle is higher.

Experimental results are illustrated in Figs. 8 and 9, where detail A gives data for HP products and detail B gives data for LP products. The time when the rupture of a thin liquid film occurs was set as the zero time. After this moment a rapid TPC line expansion was observed. The non-zero diameters of TPC line and contact angles during the period before the liquid film rupture have no physical

meaning and these values result from the image analysis where the software is unable to differentiate the thin liquid film between the bubble and solid surface.

The process of bubble adhesion in pure water is the fastest. The stable bubble position (expressed as 95% of equilibrium d_{TPC}) is achieved in 5 milliseconds. Due to the high surface tension of water both the contact angle and the ratio d_{TPC}/d_b reach the highest values (94°, 1.32 resp.). The bubble adhesion in solu-

tions of HP-DTAB and HP-SDS is also fast. Here, the stable bubble position was achieved within 20 milliseconds. The ratio d_{TPC}/d_b decreases with increasing surfactant concentration and therefore also with decreasing contact angle θ_{ea} . For the equilibrium data, we found the linear dependence between these two quantities $(d_{TPC}/d_b = 0.5518 \cdot \cos(\theta_b) + 1.0971$, R² = 0.9906). This equation is valid only for our tested solid surface and primarily shows the data consistence and mutual link between the diameter of the TPC line, the bubble contact angle and the liquid surface tension. The equilibrium d_{TPC} is influenced by many factors, but most importantly by tensions γ_{SL} and γ_{LG} . These tensions are determined by the surfactant concentration in the interfacial layers. We suppose that the ratio between the equilibrium concentrations of surfactant in bulk and on the interfaces remain stable. For pure, mono-component ionic surfactants we can find a linear dependence between the bubble adhesion efficiency and surfactant concentration, which could be expressed by surface tension or bubble contact angle.

The bubble adhesion is significantly influenced by the presence of contaminants. The period between the bubble creation on the capillary and the final collision takes a few seconds. This period is long enough to allow contaminants to approach the gas-liquid interface and influence the surface tension. In the case of contaminated SDS, the decrease of surface tension due to the SDS presence is fast and the equilibrium is reached within 1 s. An additional decrease of surface tension is caused by contaminants; the influence of dodecanol in our mixtures is visible after a few seconds (see Figs. 4 and 5, [4]). Such adsorption kinetics could be described using the diffusion-controlled adsorption model [28]. The results obtained for LP-DTAB solutions are illustrated in Fig. 8B and some of them are unexpected. The behaviour of solutions with low concentration (6.5 mmol/l and 9.7 mmol/l) is not too different from HP-DTAB. We observed an unequivocal decrease both of ratio d_{TPC}/d_b and contact angle θ_{eq} , but the bubble adhesion efficiency is still high enough for industrial needs [30]. Quite different results were observed for solutions with the DTAB concentration 13.0 mmol/l; here $d_{TPC}/d_b = 0.71$ and $\theta_{eq} = 50^\circ$. The capture of bubbles is unstable and also the TPC line expansion is much slower. On the contrary, in the solution with the highest DTAB concentration (16.2 mmol/l, which is above CMC) we found faster TPC line expansion and also more stable bubble capture. Similar results were obtained for LP-SDS (see Fig. 9B). The process of bubble adhesion was relatively fast and the bubble capture was stable in the solution with a low SDS concentration (5.2 mmol/l). In the solution with a concentration close to CMC (8.3 mmol/l) we did not even observe any bubble adhesion. For a few minutes the bubble remained beneath the surface without any motion and we did not notice either the rupture of the liquid film or the creation of the TPC line. On the other hand, we observed a slow bubble adhesion in the solution with SDS concentration 17.3 mmol/l. Here, the equilibrium was achieved after 100 ms. From these results, it is evident that the contaminants have the greatest impact in the area around CMC. This finding is consistent with the theoretical expectations. According to Ward [1], the amount of dodecanol in the monolayer reaches a maximum below the CMC.

When describing the influence of contaminants on the bubble adhesion onto the hydrophobic surface, we must firstly consider the surfactant concentrations on s-l, s-g and l-g interfaces and secondly the concentration gradients near the moving three-phase interface. The aim of this work is not the theoretical description of these processes at microscale level, but rather the mapping of fields where contaminants significantly affect the behaviour of bubbles and can unexpectedly influence the interaction of bubbles and particles. It can be stated generally that contaminants decrease the bubble adhesion efficiency when compared with mono-surfactant solutions. The contact angle is reduced by 5° to 15° and the TPC expansion is slower. This leads to the lower bubble stability of capture due to the minor contact area. In the range 0.8 CMC to CMC the influence of contaminants is crucial. The ratio d_{TPC}/d_b as well as the equilibrium contact angle are significantly lower than in the solution with a higher surfactant concentration. Under certain conditions the adhesion of bubbles does not occur. Here it was observed for LP-SDS. The liquid film is probably stabilized by the strong electrostatic repulsion of the charged surfactant layers on the liquid-gas and liquid-solid interfaces [31].

The detection of contaminant influence is commonly tricky. The simple measurement of surface tension, e.g. the ring method, could be misleading because the contaminants affect the surface tension after a longer time period. Therefore, the dynamic methods (pendant drop, maximum bubble pressure) are more useful. Also, the comparison of drop contact angles for differently concentrated solutions (below and above CMC) could give a quick guideline.

3.5. Velocity of the three-phase contact line expansion

The velocity of TPC line expansion was calculated as U_{TPC} i = $(d_{TPC,i+1} - d_{TPC,i}) / (\tau_{i+1} - \tau_i)$. The results for DTAB solutions are given in Fig. 10 where the velocity is plotted against time. For the lowest concentration 6.5 mmol/l, there is no difference in TPC expansion velocity. This means that the contaminants do not obstruct the motion of DTAB molecules. In the solution with concentration 9.7 mmol/l, we can observe a stronger influence of contaminants, which results in a slight decrease in U_{TPC}. In the solution with concentration 13 mmol/l, the TPC line motion is very slow. For the HP solution, the maximum U_{TPC} was detected 2 milliseconds later when compared with the lowest concentration and also U_{TPC} amounted to half of the maximum value. In the case of the LP solution, the TPC velocity is extremely slow. The contaminants not only reduce the surface tension but also hinder the movement of DTAB molecules in the vicinity of the TPC line. These outcomes result from a few measurements and are indicative only. In the future, we are planning a more detailed study.

4. Conclusion

In the present work we have analysed the influence of ionic surfactants on dynamics of bubble adhesion onto the hydrophobic surface. Here, the enormous influence of possible contaminants was observed. For pure, mono-component ionic surfactants, we observed a linear dependence between the surfactant concentration and bubble adhesion efficiency, which could be expressed by surface tension, bubble contact angle or the TPC line diameter. The surfactants with lower purity are usually used both in industrial applications and experiments at the pilot level. The most common contaminant is dodecanol. Its concentration in the monolayer reaches a maximum below the CMC and in case of bubble lifetimes longer than few seconds the contaminants are more surface active than the main component. The contaminants generally decrease the bubble adhesion efficiency when compared with the monosurfactant solution. Their influence is crucial in the range 0.8 CMC to CMC. Here, the surface tension is decreased below the value typical for CMC, the bubble contact angles are likewise lower and the velocity of TPC line expansion slows significantly. It may even happen that the capture of bubbles is avoided.

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Detailed experimental study of bubble adhesion on hydrophobic surface

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Abstract: This work is focused on the detailed experimental study of bubble adhesion on a hydrophobic solid surface. The frame rate 16000 fps was used in side view arrangement in order to capture in detail the three-phase contact line expansion and bubble shape changes. Experiments were done in pure water and in solutions of the anionic surfactant sodium dodecyl sulphate in low, medium and high concentrations. It was found out that the rupture of a liquid film is not symmetrical with respect to the vertical axis of the bubble symmetry. This asymmetry of TPC line formation leads to bubble surface oscillations and asymmetry in dynamic contact angles. These dynamic mechanisms are diminished with increasing surfactant concentration. The non-linearity of expansion velocity was also observed. In the case of high bubble surface mobility, the expansion velocity first decreases and after few milliseconds, the second velocity maximum emerges caused by kinetic energy dissipation. In surfactant solutions, the arising Marangoni stresses should be taken into account because the expansion velocity increases in the first moments of TPC line expansion. Existing models, such as hydrodynamic and molecular-kinetic, are not able to incorporate with bubble oscillations in pure liquids as well as the non-monotonic curve of expansion velocity profile in surfactant solutions.

Keywords: bubble-particle interaction, bubble adhesion, three-phase contact line, surfactant

1. Introduction

The interaction between bubbles and solid particles is an important mechanism in many industrial processes. The bubble-particle interaction is usually divided into three sub-processes (Yoon, 2000): a collision of bubble and particle, an adhesion and a possible detachment. When the bubble and the particle are sufficiently close together, a liquid interface film is formed between the bubble and the particle surface. The rate of the film depletion (often referred to as film drainage rate) is limited by the liquid viscosity at the beginning of the process, reaching its critical thickness. At this point, the rate starts to be influenced by the intermolecular forces acting between the molecules of the liquid and the solid particle. This phase is the most significant for the selection between hydrophobic and hydrophilic particles. Whereas in the case of hydrophilic surfaces, the intermolecular forces stabilise the liquid interface film so that the bubble never adheres to the solid surface, in the case of hydrophobic surfaces, the forces act to destabilise the film and eventually break it to form the threephase contact line (Fujasova-Zednikova et al., 2010). The liquid interface film ruptures in the case of highly hydrophobic solid surfaces, but the time of depletion depends on the stability of the film formed, its drainage kinetics and the critical thickness of its rupture (Zawala et al., 2016). Generally, the more hydrophobic the surface is, the less stable the interface film is. Since the hydrophobic surfaces show a high affinity to air, the roughness of the solid surface plays an important role as well because the surface cavities or scratches can entrap air in the form of micro- or nano-bubbles. Zawala et al. (2016) suggested that the presence of air facilitates the film rupture due to the low stability of the local liquid films between the micro- or nano-bubbles and the colliding bubble. The three-phase contact (TPC) line in pure water is then formed as a result of coalescence between submicroscopic bubbles already attached to the hydrophobic surfaces and the colliding bubble.

After the rupture of the interface film, the liquid phase begins to retreat from the solid surface due to an uneven distribution of the liquid-gas interfacial tension. The movement of the three-phase contact line is involved in both the wetting and dewetting mechanisms. Dewetting is applied in the case of bubble adhesion on a solid particle, while wetting occurs during liquid drop spreading on a solid surface. The contact line movement is driven by fluid dynamics and molecular interactions of the contacting phases. Surface tension and inertial and viscous forces influence the expansion of the TPC line. The resultant of the forces influences the curvature of the liquid-gas interface and therefore affects the shape of the bubble. The dynamic contact angle is the measure of the interface deformation at the contact point (Phan et al., 2006). The dynamic process of either wetting or dewetting can be described by the velocity of the contact line *U* which is defined as:

$$U = \frac{dr_{TPC}}{dt} \,. \tag{1}$$

where r_{TPC} is the radius of the three-phase contact line and *t* is time. As suggested by Phan et al. (2006), in the case of small bubbles, the bubble surface is assumed to remain axially symmetric with respect to the vertical axis perpendicular to the solid surface, while the centre of the TPC area is stationary during the TPC expansion. Several theoretical models have been developed to describe the TPC line expansion, relating the velocity dependence on dynamic contact angle to measurable properties such as surface and interfacial tension, liquid viscosity and static contact angle. The two main approaches are the hydrodynamic and molecular-kinetic models; the first one is rather macroscopic and discounts the role of the solid surface whereas the second one accommodates it. An alternative view is the combined model, which applies both surface and hydrodynamic factors (Schneemilch et al., 1998).

Cox (1986) established the basics of the hydrodynamic model for the wetting mechanism. It suggests that the process is dominated by the fluid viscous dissipation. Thus, the bulk viscous friction is the main resistance force for the TPC line contact motion (Ranabothu et al., 2005). The theory solves the equations governing the fluid dissipation, the continuity and Navier-Stokes equations, and relates the expansion velocity U to the dynamic contact angle θ . The main deficiency of this model is the description of the fluid motion very near to the contact line. Thus, the slip length of the nanometre scale (characteristic length scale of inner region) was introduced to describe the unique hydrodynamic mechanisms acting in close proximity of the contact line (Phan et al., 2006). The characteristic length scale of a microscopic region is usually of the order of 1 nm. One of the drawbacks of the hydrodynamic model is the means of estimating the microscopic contact angle θ_{micro} since this angle is not readily measurable. In practice the microscopic contact angle is usually replaced by the equilibrium contact angle, which can be experimentally measured (Phan et al., 2003). The velocity of expansion U and the TPC line radius r_{TPC} are given as:

$$U(t) = \frac{\gamma \left(\theta_0^3 - \theta^3(t)\right)}{9\ln(R/L) \eta} , \qquad r_{TPC}(t) = \frac{\gamma}{9\ln(R/L) \eta} \int_0^t \left(\theta_0^3 - \theta^3(t)\right) dt .$$
(2)

where, γ is the liquid surface tension, η is the liquid dynamic viscosity and the ratio R/L is the adjustable parameter. θ_0 is the equilibrium contact angle and θ is the dynamic contact angle. Use of the hydrodynamic theory has been suggested for wetting mechanism at low contact velocities (Ranabothu et al., 2005).

The second theoretical model for wetting and dewetting processes is the molecular-kinetic model. Unlike the hydrodynamic model, it eliminates the viscous dissipation but includes the solid surface characteristics. The theory is based on a statistical treatment of the transport mechanism of molecules and ions. This model assumes the energy dissipation to occur only at the moving contact line, where adsorption and desorption processes occur. The movement of the TPC line is ruled by the statistic kinetics of molecular events arising at the adsorption sites of the solid surface (Phan et al., 2006). The most common approach to the molecular-kinetic model is the one proposed by Blake and Haynes (1969), which is commonly applied to dynamic wetting. The dependence of expansion velocity on the dynamic contact angle is due to the disturbance of adsorption equilibrium, which is driven by the
changes in the local interface tensions (Phan et al., 2003). The equation for the dependence of expansion velocity on dynamic contact angle is given by (Phan et al., 2003 and 2006):

$$U(t) = 2\nu\lambda \sinh\left(\frac{\gamma\lambda^2}{2k_BT}(\cos\theta(t) - \cos\theta_0)\right).$$
(3)

The frequency v and distance of molecular displacement λ are usually not known, and therefore they have been treated as adjustable parameters. The dimension of λ can be estimated as the order of molecular dimensions (1 nm). The expected value for v is from 10⁻⁶ to 10⁻⁷ s⁻¹ (Phan et al., 2006).

Since it was shown that the two mentioned models for wetting and dewetting mechanisms do not fit the entire velocity range of experimental data, a combined molecular-hydrodynamic approach has been proposed (Phan et al., 2003 and 2006, Ranabothu et al., 2005). The dewetting hydrodynamics is used to describe the effect of fluid flow on the interface deformation far from the three-phase contact line. The microscopic contact angle θ_{micro} in the hydrodynamic model is assumed to be dependent on the expansion velocity. Molecular kinetics is then used to determine this contact angle and describe the dewetting close to the contact line. The combined model has been reported as more successful to describe the experimental data than the two previously discussed models for both wetting and dewetting mechanisms by various authors (Schneemilch et al., 1998; Ranabothu et al., 2005; Phan et al., 2006). Recently, Fetzer and Ralston (2009) studied bubble adhesion and investigated the dewetting mechanism of water on surfaces of a wide range of wettability; here the combined model was used to analyse the data. The dewetting mechanism was observed from above assuming the spherical bubble shape and the circular TPC line with the centre remaining in a stable position. The authors reported that on all studied surfaces the contact radius $r_{\rm TPC}$ initially increased quickly and then continuously slowed down until r_{TPC} reached an equilibrium value. Based on asymmetric results for λ found for advancing and receding contact angles, it was concluded that the molecular displacements are not caused by adsorption or desorption events but rather by the nanometre-scale surface heterogeneity (chemical or topographical), which influences the contact line motion in a low-velocity regime.

It is clear from the above overview that all models describing TPC line extension are based on similar principles: *i*) the liquid film break occurs on the bubble symmetry axis; *ii*) the position of the bubble's centre of gravity position is also on the vertical axis of symmetry and *iii*) the radius of TPC line gradually increases as the velocity of TPC line expansion decreases. These assumptions have not yet been experimentally verified. This project is thus focused on the detailed experimental study of bubble adhesion on a hydrophobic solid surface. We use the high-speed camera in side position in high resolution and capture frequency 16,000 fps in order to precisely capture the bubble motion and shape oscillation during the adhesion. The solutions used are demineralized water and solutions of surface active compounds.

2. Material and methods

Experiments were performed at 25 °C in pure water and in an aqueous solution of the anionic surfactant sodium dodecyl sulphate (SDS). The concentrations were 5×10-5 M (denoted as SDS low), 3.7×10-3 M (SDS medium) and 2×10-2 M (SDS high). SDS was purchased from Sigma-Aldrich Chemical Company (for ion pair chromatography, details in Basarova et al., 2017) and used as received. The experimental measurements were performed in a special glass flotation cell (50 cm height, 8 cm width and 6 cm depth). Single bubbles were created by a bubble generator at the top of a thin capillary (inner diameter 10 µm, outer diameter 375 µm; details in Hubicka et al., 2013) and after detaching from the capillary the bubble rose through the liquid to the solid particle represented by a silanized glass placed on a horizontal plane. The distance between the capillary tip and the glass surface was 20 cm and the bubbles reached the terminal rising velocity. The mechanism of bubble-particle interaction, i.e. the bubble motion before the collision with the solid particle and during the adhesion, was recorded using a high-speed digital camera Photron FastCam SA1.1 (16000 fps, resolution of 768×512 pixels) with a Navitar macro objective. Silanized glass was used as a model hydrophobic surface. The Silanization solution I was supplied by Sigma-Aldrich (5% solution of dimethyldichlorosilane in heptane, CAS No. 75-78-5). The glass material (microscopic slides) was cleaned in a boiling mixture of sulphuric acid and hydrogen peroxide (1:1) for 1 min, then rinsed several times with distilled water

and dried. The slides were dipped into the silanization solution for 24 h then rinsed firstly with pure heptane, then with acetone and ethanol in order to remove all organic residues, and finally, they were dried. The contact angle for pure water drops was 98.2°.

At least five video sequences were captured for every size of the bubble. The image analysis was done using the NIS-Elements Advanced Research software. The video series were converted to the nd2 format and saved with the relevant calibration (approx. 2.8 µm per pixel). All the sequences were qualitatively observed with regard to possible bouncing, bubble shape deformation and the symmetry of three-phase contact line expansion. The bubble diameter D_{b} , the time of liquid interface film depletion t_{dep} and the final equilibrium contact angle θ_0 were measured for every sequence. The development of the diameter of TPC line d_{TPC} over time was evaluated for each sequence as well. The dynamic contact angle θ and the position of bubble gravity centre changing with time were evaluated only for one selected sequence for each experimental solution since these analyses were time demanding due to the length of the processed sequences (5000 frames). The software functions centreX and centreY were used for the determination of bubble centre. The velocity of TPC expansion was calculated as:

$$U_{i} = \frac{d_{TPC}(t_{i+1}) - d_{TPC}(t_{i})}{2 \cdot (t_{i+1} - t_{i})}.$$
(4)

The dynamic surface tension of all solutions at 25 °C was measured using the Krűss tensiometer BP100 employing the maximum bubble pressure method. It characterises the adsorption of surfaceactive molecules on a liquid-gas interface. The maximum bubble pressure measurement method gives the dependence of surface tension on surface age. The surface tension of water at 25 °C is 72.4 mN·m⁻¹ and does not depend on the bubble age (see Fig. 1). In solutions of surfactants, the surface tension changes over time. A freshly formed liquid-gas interface has a surface tension very close to that of a solvent. Over a period of time, surface-active molecules adsorb onto the interface. The surface tension decays to its equilibrium value and this period of time can range from milliseconds to days depending on the surfactant type and concentration. SDS has a simple molecule, it adsorbs fast from the subsurface to the interface and the diffusion-controlled adsorption model could be used for its description (Basarova et al., 2017). The decrease of surface tension is evident already after 10 ms of surface age as seen in Fig. 1, except for a lowest concentration of SDS, where the decrease is observable at a surface age of 80 ms. The measurement was limited to a surface age of 100 s and both solutions with low SDS concentrations and high SDS concentrations reached their equilibrium surface tension whereas, in the case of medium SDS concentration, the surface tension is further expected to slightly decrease. The surface tension of all studied solutions is sufficiently different and thus the influence of surface active agents on bubble adhesion dynamics could be discussed for low, medium and high surfactant concentration.



Fig. 1. Dynamic surface tension measured by maximum bubble pressure method. Concentrations of SDS solutions are 5×10⁻⁵ M (SDS low), 3.7×10⁻³ M (SDS medium) and 2×10⁻² M (SDS high)

3. Results and discussion

The bubble adhesion was captured by a high-speed camera at 16,000 fps and about 5,000 frames were saved for each image sequence. That captures around 300 milliseconds of the process within which the bubble collided with the solid surface, the interface film formed, depleted and ruptured and the three-phase contact line expanded to equilibrium. Each of these steps had a distinct behaviour for different surfactant concentrations. The characteristics of bubble adhesion onto hydrophobic silanized glass in water and each SDS solution are thus discussed separately.

3.1 Pure water

Figure 2 shows the different steps of bubble interaction ($D_b = 0.705$ mm) with a particle of infinite radius and a hydrophobic surface. The bubble rises in the solution towards the solid particle (WC1) and it collides with the particle (WC2). After the collision, the bubble is deformed; higher speed leads to a bounce (WC3), in some cases, even to multiple bounces. Subsequently, the bubble returns to its own original shape and a liquid film is created between the bubble and the particle (WC4) (the film itself is usually not visible on the captured images because of the pixel resolution, wavy character of light and aperture angle). The film gradually depletes and ruptures. Image W0 illustrates the situation just before the film rupture. Note that this time (t = 0 ms) is set as the time of the rupture of the liquid interface film, therefore the images capturing the bubble-particle collision and liquid interface film depletion are indicated with negative times. The formation of the three-phase contact (TPC) line is visible after 0.0625 seconds (W1). The TPC line expansion continues (W2) together with significant bubble shape deformation, where the bubble is first prolonged (W3, W4) and then compressed (W5 -W7) in the vertical direction. While the diameter of the three-phase contact line does not change significantly anymore, the bubble shape deformation is still observable (W8 - W10). The bubble shape deformation during expansion could be described as a form of bouncing while keeping the threephase contact. We assume that this is caused by residual kinetic energy dissipation and full bubble surface mobility which allows the interfacial oscillations and waves on bubble surface. Image W11 presents the bubble at equilibrium, where both the diameter of the TPC line and the bubble shape do not change anymore.



Fig. 2. A series of photos illustrating a course and outcome of the bubble ($D_b = 0.705$ mm) adhesion onto the solid surface in pure water

The bubble movement described above can be quantified as the position of the bubble gravity centre changing with time. Figure 3A shows the relative change of the bubble gravity centre position (centre Y) in the vertical direction over time. Note that the Y coordinate increases opposite to the bubble movement as shown in Fig. 2 and in this graph, this value is normalised by the position at t = 0 milliseconds. Both the above discussed bouncing after the bubble-particle collision and the bubble shape deformation during the TPC line expansion can be represented by the sinusoidal parts of the graph. The bubble gravity centre motion during the first moments of the TPC line expansion is shown in more detail in Fig. 3B.



Fig. 3. The bubble gravity centre's motion in the vertical direction. The highlighted points correspond to images in Fig. 2

The diameter of the three-phase contact line d_{TPC} was measured for every image of the video sequence and the expansion velocity U was calculated in each time step according to eq. 4. The time dependence of both quantities for the individual bubble to before is shown in Fig. 4A. The non-zero value of d_{TPC} at t = 0 ms does not have a physical meaning as the three-phase contact is not formed yet. The TPC line in water expands very quickly; the velocity reaches its maximum (almost $0.5 \text{ m} \cdot \text{s}^{-1}$) in the first captured moment (the visible change between images W1/W2). The TPC line continues to grow but with a decreasing velocity. At around 1.3 ms the expansion velocity increases again and its peak is observable with its maximum at 1.375 ms (the change between images W6/W7). We assume that this acceleration is caused by the bubble shape deformation. As the bubble is being compressed (W6 and W7 in Fig. 2), the bubble mass is forced to shift to the horizontal direction, therefore the three-phase contact line expands faster. As the TPC line diameter reaches a stable value, the expansion velocity becomes zero (W8). Even though the bubble shape continues to change after this point, it does not affect the size of TPC line significantly anymore. Figure 4B shows the expansion velocity for different bubble sizes in water. The points represent the average value measured from 5-6 sequences. Although it seems that the bubble size does not actually influence the extent of the velocity, as both peaks are of the same height for different bubble diameters, it significantly influences the timing. The smaller the bubble, the earlier the velocity peak appears and the earlier the equilibrium diameter (zero velocity) is reached. Individual bubble behaviour was observed and mathematically described by Zawala et al. (2016). To conclude, typical features of bubble adhesion in pure water are *i*) visible bouncing after the collision, *ii*) fast TPC line expansion (finished in 2 ms), *iii*) bubble shape deformation during the adhesion and iv) additional maximum on velocity profile.



Fig. 4. TPC expansion velocity and diameter of the TPC line expansion in pure water for a bubble with diameter 0.705 mm (detail A) and average values for bubbles with diameters 0.70 mm, 0.74 mm and 0.85 mm (detail B)

The time-dependence pattern of dynamic contact angles matches the course of d_{TPC} (Fig. 4A). Firstly we observed a fast increase of contact angle values and then, after 1 ms, we observed the oscillations between left and right angles reaching up to 6°. Only insignificant increase was observed after 3 ms which goes together with negligible TPC expansion velocity. The average equilibrium contact angle was 98° and this value did not change with changing bubble size.

3.2 Solutions with low surfactant concentration

Figure 5 illustrates the bubble adhesion process ($D_b = 0.865$ mm) in a solution of a very low concentration of SDS (5×10⁻⁵ M). It shows representative images of bubble adhesion at indicated times before (SLC1-SL0) and after (SL1-SL10) the liquid interface film rupture. The bubble gravity centre movement in the vertical direction is shown in Fig. 6A. The bubble rises in the surfactant solution (SLC1), it collides with the solid surface, the bubble shape being deformed (SLC2), and it slightly rebounds (SLC3) before colliding with the solid surface again (SLC4). This phase does not differ significantly from the collision behaviour in pure water; therefore, we can assume that the leading pole of the bubble is completely free of surfactant molecules, which seems to be a reasonable assumption considering the very low surfactant concentration. The three phase contact line forming from the right side can be observed (with a close look) in image SL1. Afterwards, the TPC line continues to expand only on the right side (SL2). The left side of the TPC line starts to move after another 0.5 milliseconds. A slight bubble shape deformation is visible (SL4, SL5) and an oscillation of the bubble gravity centre is observed (Fig. 6B). When compared with the results for pure water (see Fig. 3), we can observe a substantial suppression and time extension of the bubble oscillations in the vertical direction. This behaviour is typical for solutions with low surfactant concentration.



Fig. 5. Sequence of photos illustrating a course and outcome of the bubble (D_b = 0.865 mm) adhesion onto the solid surface in aqueous solution of SDS (low concentration 5×10-5 M)



Fig. 6. The bubble gravity centre motion in the vertical direction in an aqueous solution of SDS (low concentration 5×10⁻⁵ M). The highlighted points correspond to the images in Fig. 5

The fact that the TPC line expansion does not start at the centre of the bubble contact and that the expansion is not symmetric was observed in many image sequences of all the studied solutions, including pure water. In fact, the TPC line expansion started from the centre only in less than 20% of cases. We assume that the positioning of the liquid interface film rupture is related to the inhomogeneity given by the presence of microscopic bubbles and solid surface roughness (Krasowska and Malysa, 2007). During these oscillations, dynamic contact angles measured on right and left side of the bubble vary by 6°.

The time dependence of both the diameter of three-phase contact line and the expansion velocity U for the individual bubble is shown in Fig.7A. The TPC line expansion accelerates (SL2) after 0.5 ms. The velocity then reaches its maximum after 1 ms of expansion (SL4). After 2 ms a second peak can be noticed (SL5), but this is in no case as significant as in water. This is in agreement with the previously made conclusion that the second peak is caused by a bubble shape deformation. The expansion comes to a slow phase around 3.5 ms (SL7). After this point the TPC line diameter increases very slowly and taking into account the pixel resolution and calibration, the measurable change in d_{TPC} is not observed at each time step and therefore the expansion velocity U appears to fluctuate even though the actual velocity is gradually decreasing to zero. Image SL10 shows the bubble after reaching the three-phase contact equilibrium. Figure 7B shows the expansion velocity for two bubble sizes. Similarly to the results in pure water, one can observe an influence of bubble size. The position of the second peak of velocity maximum was observed earlier for the smaller bubble. Moreover, we observed the different initial expansion velocity, which was probably influenced by the different surfactant coverage of the bubble surface due to the different bubble size. When compared with pure water, the velocity of the TPC line expansion has dropped to roughly half and thus the adhesion time has increased. The average equilibrium contact angle was 94° and this value did not depend on bubble size. The typical features of bubble adhesion are: i) a moderate bubble shape deformation during the adhesion and ii) two maxima in the velocity profile.



Fig. 7. TPC expansion velocity and diameter of TPC line expansion for a bubble with diameter 0.865 mm (detail A) and average values for bubbles with diameters 0.77 mm and 0.88 mm (detail B). Low SDS concentration

3.3 Solutions with medium surfactant concentration

Figure 8 shows the different steps of bubble adhesion ($D_b = 0.926$ mm) onto the hydrophobic surface in the aqueous solution of SDS with the concentration 3.7×10^{-3} M. This surfactant concentration is still below its critical micelle concentration. The figure shows representative images of the bubble adhesion at indicated times before (SMC1-SM0) and after (SM1-SM6) the liquid interface film rupture.

The bubble gravity centre movement in the Y direction (centre Y normalised by the centre Y at t = 0) is shown in Figure 9. The bubble rises towards the solid particle (SMC1) and collides, the bubble shape being deformed (SMC2). The bouncing is limited; the bubble moves back from the surface only slightly (SMC3) as seen on the bubble gravity centre movement. This motion is influenced by the presence of surfactant molecules, which decreases the surface elasticity. The liquid interface film ruptures (SM0) and the three-phase contact line starts to expand. The expansion starts on the left side

(SM1, SM2) and the right side expands after another 1.5 ms (see Fig. 9B). The bubble shape deformation (SM3) is thus caused by the non-symmetry of the expansion. The effect of the non-symmetrical TPC line expansion on the dynamic contact angles is crucial and the contact angles on the left and right side can vary by up to 5 degrees. Later, only small oscillations are observable in the vertical movement of the bubble gravity centre (SM4) and the bubble centre reaches its stable position after 15 ms (SM5, SM6) as seen in Fig. 9B. The motion in the horizontal direction follows due to the inertial force. Please note the different magnitudes of the main and minor vertical axes. Whereas the distance between SM2 and SM4 position in the vertical direction is 100 μ m, the same distance in the horizontal direction is only 30 μ m. A similar horizontal motion of bubble centre was observed for majority of bubbles. The displacement of bubble centre in water did not exceed 20 μ m, while in SDS solutions the average horizontal distance ranged from 30 to 40 μ m.



Fig. 8. Sequence of photos illustrating a course and outcome of the bubble (D_b = 0.926 mm) adhesion onto the solid surface in aqueous solution of SDS (medium concentration 3.7×10^{-3} M)



Fig. 9. The bubble gravity centre motion in the vertical direction in aqueous solution of SDS (medium concentration 3.7×10⁻³ M). Detail B: the relative vertical and horizontal bubble gravity centres motion after the TPC line formation. The highlighted points correspond to the images in Fig. 8

The progress of the TPC line diameter and the expansion velocity is shown in Figure 10A. The diameter expands slowly in the first millisecond, then the expansion velocity increases and the TPC line expands at a maximum velocity around 2 ms after the liquid film rupture (SM2, SM3). Afterwards, the expansion velocity decreases and it comes to a slow phase around 5 ms (SM4). The second increase of the expansion velocity is visible only for the biggest bubble at 4 ms. Data for three bubble sizes are summarised in detail B. The course of velocity is similar for all studied bubbles. The velocity decreases significantly up to $0.1 \text{ m} \cdot \text{s}^{-1}$ maximum and the adhesion time is prolonged to 10 ms. The dynamic contact angles increase gradually following the pattern of d_{TPC} . The average equilibrium contact angle was 82°. By analysing all the image sequences captured for medium SDS concentration it

can be concluded that the typical features of bubble adhesion to hydrophobic surface in SDS concentration below CMC are: *i*) a hindered bouncing after the collision due to presence of surfactant molecules, *ii*) an asymmetric rupture of the liquid interface film (the TPC line expands at one side), and *iii*) an expansion velocity increase within the first moments of the TPC line expansion and its maximum at 1.5 ms.



Fig. 10. Bubble velocity and diameter of the TPC line expansion for a bubble with diameter 0.926 mm (detail A) and average values for bubbles with diameters 0.79 mm, 0.83 mm and 0.92 mm (detail B). Medium SDS concentration

3.4 Solutions with medium surfactant concentration

Figure 11 illustrates the bubble adhesion process ($D_b = 0.864$ mm) in a solution with high concentration of SDS (2×10⁻² M), which is above the critical micelle concentration. It shows representative images of the bubble adhesion at indicated times before (SHC1-SH0) and after (SH1-SH5) the liquid interface film rupture.



Fig. 11. Sequence of photos illustrating a course and outcome of the bubble (D_b = 0.864 mm) adhesion onto the solid surface in aqueous solution of SDS (high concentration 2×10-2 M).

The bubble gravity centre movement in the Y direction (centre Y normalised by the centre Y at t = 0) is shown in Fig. 12. The bubble rising and its collision with the solid surface was not captured because the time lapse between the collision and the actual formation of the TPC line was longer than is possible to capture; it varied between 5 and 30 seconds. No bubble bouncing was observed (SHC1, SHC2). The extended time of the liquid interface film depletion is caused by the high concentration of surfactant molecules, which stabilises the interface film (Malysa et al., 2005). The variation in the depletion time could be caused by a different distribution of microscopic bubbles, which corresponds to the distribution of surface imperfections. The image SH0 shows the bubble right before the rupture of the interface film. The TPC line then starts to expand from the left side (SH1), the right side slowly joining only after 2 ms. The bubble regains symmetry after 5 ms (SH3) and slowly continues to expand. The expansion is still not finished after 15 ms (SH4) and the equilibrium TPC line diameter is reached only after 40 ms (SH5). No bubble shape deformation is detected and the bubble centre moves steadily towards the solid surface. The high concentration of surface active molecules in the solution is assumed to result in the bubble being completely covered by surfactant molecules. The adsorption and desorption exchange of the surfactant molecules between the bubble and the solid surface then

control the rate of the TPC line expansion. The time-dependence of the expansion velocity U is shown in Fig. 12. The expansion of the TPC line is similar to that of Fig 10A and it is even more gradual. Since the expansion is very slow and the TPC line diameter changes only within a few μ m between the two images, the expansion velocity was calculated over a longer time step 0.5 ms to better capture the actual progress of the expansion velocity. The expansion velocity increases during the first 3 ms of the expansion when it reaches its maximum (SH2). Afterwards, the expansion starts to slow down at 6 ms and slow phase is reached after approximately 20 ms of expansion.



Fig.12. TPC expansion velocity and the relative bubble gravity centre motion in the vertical direction for a bubble with diameter 0.864 mm (detail A) and average values for bubbles with diameters 0.71 mm, 0.74 mm and 0.87 mm (detail B). High SDS concentration

Data for three bubble sizes are summarised in detail B. The course of velocity is similar for all studied bubbles. The maximum value 0.02 m·s⁻¹ was reached after 5 ms and the whole adhesion time prolonged to more than 20 ms. The average equilibrium contact angle was 69° and its value did not depend on bubble size. The typical features of bubble adhesion in a high concentration of surfactant are: i) no bouncing after the collision or during the bubble adhesion, ii) liquid film stabilisation and iii) a very slow TPC line expansion.

3.5. Applicability of existing theoretical models

The hydrodynamic and the molecular-kinetic models are two alternative approaches usually used for the description of the bubble TPC line expansion. In both cases, the driving force of this process is the difference between the dynamic and the equilibrium contact angles (Eqs. 2 and 3). The suitability of these models has been investigated by many researchers and the bubble adhesion process was observed either from the side view or from above, but with relatively low image frame rate. The limited frame rate did not allow direct calculation of expansion velocity and most of the papers studied the dependency of the TPC line radius on the dynamic contact angles. The studies also assumed that in the case of small bubbles ($D_b < 1 \text{ mm}$), the bubble surface remains axially symmetric and the radial position of the TPC line is equal to the radius r_{TPC} . Moreover, demineralized water was used as a liquid medium in all of the published works. None of these models can deal with a liquid containing surfactants.

This work offers a new opportunity to observe the bubble adhesion process in a very detailed experimental study and thus it offers the comparison of the above-mentioned theoretical assumptions with the reality. Bubble adhesion in pure water and in solutions of surface-active agents was described in detail in the previous chapters. The main experimental observations can be summarised in the following points:

i) The rupture of a liquid film is not symmetrical with respect to the vertical axis of the bubble symmetry. This finding is in accordance with the conclusion of Chan et al. (2011), who proved that the liquid film becomes the thinnest close to the apparent contact line.

ii) The asymmetry of the TPC line formation leads to bubble surface oscillations and asymmetry in dynamic contact angles. For mobile surfaces, the uneven motion of the TPC line causes the change of boundary conditions. Due to the gradual kinetic energy dissipation, we can observe bubble shape oscillations both in the vertical and horizontal direction. Similar linear oscillations and irrotational flow during the bubble contact with the solid surface were described by Vejrazka et al. (2013). When surface-active agents are captured at the liquid-gas interface, the viscoelasticity of the bubble surface decreases significantly and the shape oscillations are dampened.

iii) The expansion velocity increases in the first moments of the TPC line expansion and in a case of a high surface mobility we can observe a second velocity maximum. The increase of expansion velocity after the TPC line formation was observed in solutions with surface-active agents. Due to a sufficient time interval between the bubble collision with the surface and the creation of the TPC contact, we expect the bubble surface to be uniformly covered by surfactant molecules. After the TPC line creation, the arising Marangoni stresses should be taken into account. The pure water-air interface is mobile and cannot withstand shear stress tangential to the air-water interface. In the presence of surfactants, the situation changes because gradients in the surface excess of surfactants can cause an effective no-slip boundary condition. At the TPC line, the solid-liquid and the air-liquid interfaces merge. In close proximity, where the distance between the solid-liquid and the liquid-vapour interface is below 100 nm, the surface force acts between the two interfaces. Merging would be delayed if a long-range repulsive surface force acted between the interfaces. Here, the charged head groups of the surfactants adsorbed at both interfaces would lead to an electrostatic double-layer repulsion. This long-range repulsion would keep the interfaces apart and delay the dewetting on the receding side (Fell et al., 2011). Thus the resulting gradient in surface tension would slow down the drainage of the liquid film.

To conclude, the mentioned simple theoretical models in their present form are not applicable to describe the three-phase contact line expansion. In the case of pure liquids, they are not able to incorporate the asymmetry of the liquid film rupture leading to bubble shape oscillations. In the case of bubble adhesion in surfactant solutions, the models do not consider the dynamic surface tension and the surfactant concentration gradient near the moving TPC line.

4. Conclusions

Bubble adhesion on a hydrophobic surface is significantly influenced by the bubble shape oscillations, which are diminished by increasing surfactant concentration. Firstly, the rupture of a liquid film is not symmetrical with respect to the vertical axis of the bubble symmetry. This asymmetry of the TPC line formation leads to bubble surface oscillations both in vertical and horizontal directions and also causes the asymmetry in dynamic contact angles. Furthermore, a non-linearity of the expansion velocity profile was observed. In pure water, i.e. in the case of full bubble surface mobility, the velocity of the three-phase contact line expansion first decreases. Due to the oscillations and kinetic energy dissipation, the second velocity maximum arises after few milliseconds. In surfactant solutions, the arising Marangoni stresses should be taken into account because the expansion velocity increases in the first moments of the TPC line expansion. Theoretical models, such as the hydrodynamic and the molecular-kinetic models are not able to incorporate the bubble oscillations in pure liquids and the non-monotonic curve of the expansion velocity profile in surfactant solutions.

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Three-phase contact line expansion during air bubble attachment to hydrophobic solid surface – experiment and modeling

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Abstract: Kinetics of spreading of the three-phase contact hole (dewetting) formed by an air bubble colliding with hydrophobic solid surface, after rupture of intervening liquid film, was studied both experimentally and numerically. During experiments it was found that evolution of the TPC line diameter with time occurs with characteristic S-shaped trend which, in consequence, causing rather unexpected maxima at the TPC line spreading velocity curves. It was determined that position of this maximum appears after 1-2 ms after TPC hole formation and its position (in respect to time) depends on the bubble diameter. In solution of surface-active substance this maximum was much smoother and longer. By means of complementary numerical calculations the source of maxima existence and differences in their position and shapes were explained. It was concluded that this effect has only hydrodynamic origin, caused by different course of bubble shape pulsations during TPC line formation and spreading, which depends on degree of liquid/gas interface immobilization (fluidity retardation).

Keywords: three-phase contact, bubble, attachment, dewetting, simulations

1. Introduction

The attachment of bubbles onto a solid surface plays a critical role in many industrial applications. The bubble adhesion onto the hydrophobic particle and the stability of the created unit determine the effectiveness of the interaction process. The bubble attachment consists of two terms: (1) the thinning of liquid film to a critical thickness where rupture of the liquid film begins; and (2) the expansion of the three-phase contact line to form a stable wetting perimeter (Nguyen et al., 1997). This perimeter is usually known as the three-phase contact line (TPC line). After the formation of the TPC line its movement can be observed. Historically, literature mentions two main approaches when dealing with the kinetics of the TPC line based either on the hydrodynamic (Huh and Scriven, 1971; Cox, 1986) or molecular-kinetic theories (Yarnold and Mason, 1949; Blake and Haynes, 1969). The presence of surfactants may significantly affect the kinetics of this process (Kosior et al., 2013; Krasowska et al., 2009; Zawala et al., 2015). The TPC line dynamics is influenced by the surfactant adsorption on solid-liquid, solid-gas and liquid-gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration (Radulovic et al., 2013). Surfactants also damp significantly the bubble shape oscillations, because they decrease the elasticity of interface (Vobecka et al., 2012).

In case of pure liquids, the liquid phase (after the rupture of the interface film) begins to retreat from the solid surface due to an uneven distribution of the liquid-gas interfacial tension (surface tension gradients). The contact line movement is driven by fluid dynamics, but surface tension and inertial and viscous forces influence the expansion of the TPC line too. The resultant of the forces influences the curvature of the liquid-gas interface and therefore affects the shape of the bubble. At first glance, the bubble adhesion (dewetting process) is similar to the drop spreading (wetting). The spreading process is dominated by the fluid viscous dissipation and the bulk viscous friction is usually the main resistance force for the TPC line contact motion (Ranabothu et al., 2005). Here, the theory solves the equations

governing the fluid dissipation, the continuity and Navier-Stokes equations. In the case of bubble adhesion, we have to consider also additional forces resulting from quite violent bubble shape pulsations. These oscillations were observed experimentally in case of bubbles with mobile surface (Basarova and Souskova, 2018). Immobilization of the bubble surface, e.g. by the addition of a surfactant, results in the suppression of bubble shape oscillations.

In this project, kinetics of the TPC line expansion during bubble collision and rupture at hydrophobic solid surface was studied by means of numerical simulations, both for completely mobile (slip) and fully immobilized (no-slip) liquid/gas interface. The obtained results were compared with experimental data obtained in corresponding conditions. The primary focus was put on explanation of origin of rather unexpected characteristic peaks observed for TPC line velocity vs. time dependence. It was found that position of these peaks depends on bubble radius and liquid/gas interface properties. Thanks to the simulations, the mechanism of this effect was discussed and explanation for surprising trends of the TPC line velocity variations was proposed.

2. Materials and methods

2.1. Experiments

The experimental measurements were performed in a special glass cell (rectangular cross-section, 30 cm height, 8 cm width and 6 cm depth). Single bubbles were created by a bubble generator at the top of a thin capillary with the inner diameter 10 µm (Hubicka et al., 2013). The resulting bubble diameter 0.70 and 0.85 mm was adjusted by control of the bubble growing time. After detaching from the capillary, the bubble rose through the liquid to the horizontal solid plate. Silanized glass was used as a model hydrophobic surface (Basarova and Souskova, 2018). The distance between the capillary tip and the solid surface was 20 cm, i.e. was far enough for the rising bubble to reach its terminal velocity. The phenomena occurring during the bubble-solid surface interactions, i.e. the bubble motion before and after the collision with the solid particle as well as during the adhesion, was recorded using a highspeed digital camera Photron FastCam SA1.1 (16000 fps, resolution of 1024×1024 pixels, calibration 2.8 µm per pixel) with a Navitar macro objective. At least five video sequences were captured for every size of the bubble. The image analysis was done using the NIS-Elements Advanced Research software. All the sequences were qualitatively observed with regard to possible bouncing, bubble shape deformation and the symmetry of three-phase contact line expansion. The development of the diameter of TPC line (d_{TPC}) over time and variations in the vertical position of the bubble bottom apex (y_{bottom}) were evaluated for each sequence. The bubble diameter (d_b) and the final equilibrium contact angle (θ_b) were measured for every sequence as well. The velocity of TPC expansion (U_{TPC}) was calculated as:

$$U_{TPC(i)} = \frac{d_{TPC(t_{i+1})} - d_{TPC(t_i)}}{(t_{i+1} - t_i)} \tag{1}$$

where $d_{TPC(t_{i+1})}$ and $d_{TPC(t_i)}$ were TPC line diameters measured for two subsequent frames from the recorded movies. The time step $(t_{i+1} - t_i)$ in the case of water was 0.0625 ms, while in SDS solutions, due to slower expansion of TPC line, was equal to 0.25 ms.

Experiments were performed at 25 °C in pure water and in an aqueous solution of the anionic surfactant sodium dodecyl sulphate (SDS) at concentration 2×10⁻² mol·dm⁻³. This concentration is above the critical micelle concentration equal to 8×10⁻³ mol·dm⁻³. SDS was purchased from Sigma-Aldrich Chemical Company (for ion pair chromatography, details in Basarova et al., 2017) and used as received. The surface tension of water at 25°C was 72.4 mN·m⁻¹. In case of SDS, we measured the dynamic surface tension using the Krűss tenziometer BP100 employing the maximum bubble pressure method. After 1 second, we observed the equilibrium and the surface tension was 38.5 mN·m⁻¹.

2.2. Numerical calculations

To reproduce experimental conditions, phenomena occurring during bubble attachment to the hydrophobic solid wall immersed in liquid phase was calculated numerically by solving the governing equations, describing the conservation of momentum and mass of an incompressible, viscous liquid in the form (Popinet, 2009):

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u} \cdot \nabla \boldsymbol{u}\right) = -\nabla \mathbf{p} + \nabla \cdot (2\mu \mathbf{Q}) + \sigma \kappa \delta_s \boldsymbol{n}$$
⁽²⁾

$$\nabla \cdot \boldsymbol{u} = 0 \tag{3}$$

using spatial discretization and numerical scheme described in details in (Popinet, 2003; Popinet, 2009; Fuster et al., 2009), where **Q** is a deformation tensor defined as:

$$\boldsymbol{Q} = \frac{1}{2} \left(\nabla \boldsymbol{u} + (\boldsymbol{u})^T \right) \tag{4}$$

while $u = [u_x, u_r]$ is the fluid velocity vector, ρ is the density and μ is the viscosity of the fluid, p is a pressure, t is time, σ is surface tension, δ_s is a Dirac distribution function (expressing the fact that the surface tension term is concentrated at the interface), while κ and n are the curvature and normal unit vector to the interface, respectively.

Fig. 1 presents scheme of the computational domain. The calculations were performed using a twodimensional, axi-symmetrical, cylindrical coordinate system. Radius of the computational domain (*L*) was equal to 2 mm. A spherical bubble of diameter $d_b = 2r_b$ (adjusted according to the experiment) was placed beneath the horizontal, no-slip, solid wall. Slip boundary conditions were assumed at the bottom, left and right boundaries to minimize the wall effects. For all computational domain walls, Dirichlet boundary conditions were applied. The computational domain was spatially discretized using square finite volumes called cells, which were hierarchically organized as *quadtree* (Popinet, 2003). An adaptive refinement algorithm (AMR) was applied to adjust the spatial discretization to follow the scale and temporal evolution of the flow structures. Such an approach implies that the computational mesh size varies in the domain. The grid size depends on refinement level and is directly related to the *L* value (Popinet, 2003; Zawala, 2016). The AMR implies also that the finest grid cell can be found at the liquid/gas interface and in its vicinity. In our calculations, for *L* = 2 mm and refinement level equal to 9, the smallest grid cell was equal to 3.9 μ m. As was shown elsewhere (Zawala, 2016) for *L* = 2 mm this refinement level is enough for computational results convergence.



Fig. 1. Scheme of the computational domain

The distance of the bubble top apex to the solid/liquid interface, i.e. initial thickness of the liquid film (*h*), was set to be equal to 35 μ m. This thickness resulted from numerical reasons - a bubble has to be located at the distance equal to several computational cells from the solid/liquid interface to assure stability of calculations. The density of the liquid and gas were 1000 and 1.3 kg/m³, respectively, i.e. equal to density of water and air. Similarly, the dynamic viscosity of liquid and gas was taken as 1×10⁻³ and 18×10⁻⁶ Pa·s, respectively. Similar to experimental conditions, the surface tension was assumed to be equal 72.4 mN·m⁻¹. The contact angle of the solid surface depended on the level of refinement of the solid boundary (Afkhami et al. 2009) and, under chosen computational conditions, was around 80° for bubble with fully mobile interface. To take into account bubble surface immobilization by the presence of surfactant adsorption layer, the original volume of fluid algorithm was modified. Keeping all other physicochemical parameters of the system constant, different viscosity value at the liquid/bubble interface (surface viscosity), implying secondary tangential stresses near the interface, were used in

calculations. This approach simulated bubble surface fluidity retardation in surface-active substance solution of high concentration (Zawala et al. 2016). The total kinetic energy of the system was calculated using the formula (Zawala 2016):

$$T = \frac{1}{2} \int 2\pi r \rho \boldsymbol{u} \, dx \, dr \tag{5}$$

3. Results and discussion

3.1. Experimental determination of the TPC line spreading kinetics in pure water and surfactant solutions

Fig. 2 shows the bubble adhesion ($d_b = 0.705$ mm) to the hydrophobic solid surface in pure water. The first image at t = 0 ms illustrates the situation just before the film rupture. The bubble sits at the solid surface practically motionless, after complete dissipation of its kinetic energy, related to bouncing and associated shape oscillations. The initial zero time is set as the time of the rupture of the liquid interface film and it was set on the basis of visual observation together with the calculated change of d_{TPC} . The formation of the three-phase contact line is visible after 0.0625 seconds (camera time step) on the second shot. The TPC line expansion continues together with significant bubble shape deformation, where the bubble vertical diameter is firstly extended and then compressed. While the diameter of the three-phase contact line does not change significantly anymore, the bubble shape deformation is still observable. The bubble shape deformation during expansion could be described as a form of bouncing while keeping the three-phase contact (liquid/gas interface pulsates). The images illustrate the bubble adhesion process during the first three milliseconds. Even after this time there were visible some oscillations, but the shape of the bubble did not change too much. The whole sequence consists of 5000 images including collision process and final equilibrium.



Fig. 2. A series of photos illustrating the adhesion of the bubble (d_b = 0.705 mm) onto the hydrophobic solid surface in pure water. The time interval between individual shots is 0.0625 ms

The bubble adhesion illustrated above can be characterised quantitatively using variations in diameter of the TPC line (d_{TPC}), velocity of the TPC line expansion (U_{TPC}) and the position of the bubble bottom coordinate (y_{bottom}). Fig. 3 presents the data which were calculated for the bubble adhesion process presented in Fig. 2. The bubble diameter (before liquid film rupture – first photo in Fig. 2) is

0.705 mm and the time step between individual images is 0.0625 milliseconds. We observed bubble flattening due to buoyancy before the formation of TPC line and thus y_{bottom} (at t=0 ms) is smaller than d_b . The non-zero value of d_{TPC} at t = 0 ms does not have a physical meaning and it is a result of computer data processing - this is the diameter of liquid film (contact between bubble and solid surface) just before its rupture. The TPC line expands very quickly; the velocity reaches its maximum in the first captured moment (0.1 ms). The TPC line continues to expand but with a decreasing velocity. At around 1.3 ms the expansion velocity increases again and unexpected second peak can be observed with its maximum at t = 1.4 ms. On the d_{TPC} curve, one can see that this effect is associated with a small S-shape course. After that, the TPC line diameter reaches a stable value and the expansion velocity becomes zero. This whole process from TPC line formation to stable TPC position took 1.7 ms. Even though the bubble shape continues to change after this point (see left image in Fig. 3) it does not affect the length of TPC line significantly anymore. Also the contact angle does not change. The equilibrium contact angle in this case was 99.5°. To conclude, during the first 2 ms after liquid film rupture we can observe quick TPC line expansion connected with the change of bubble shape. Fig. 3 shows also the change of the bubble bottom apex position (y_{bottom}) in the vertical direction over time. In first 0.5 milliseconds, no change was observed even though both d_{TPC} and U_{TPC} change dramatically. During the quick bubble adhesion part the bottom apex position decreases significantly due to the bubble flattening. After that, we can observe typical oscillations. The period between the individual peaks is 1.2 ms and the whole process is muted after 20 ms.



Fig. 3. The time dependence of the diameter of the TPC line (left), TPC expansion velocity (middle) and bubble bottom apex position (right) in pure water for a bubble with diameter 0.705. The time interval between individual points is 0.0625 ms

Fig. 4 shows the TPC diameter and expansion velocity for two different bubble sizes in water. The points represent the average value measured from 3-4 sequences. The courses of the two monitored quantities are similar. The TPC diameter increases with bubble size. The ratio d_{TPC}/d_b remains constant as the wetting angle does not change. The average value of the contact angle was 97.8° ± 2.2°. Although it seems that the bubble size does not significantly influence the extent of the velocity, it significantly influences the timing. The smaller the bubble, the earlier the velocity peak appears and the earlier the equilibrium diameter (zero velocity) is reached. To conclude, typical features of bubble adhesion in pure water are i) fast TPC line expansion (finished in 2 ms), ii) bubble shape deformation during the adhesion, iii) additional maximum on velocity profile and iv) bubble shape oscillations.

The second part of experiments was done in aqueous solution of the surface-active agent SDS. The concentration is 2×10^{-2} mol·l⁻¹ which is above the critical micelle concentration. Under these conditions we assume a fully immobile surface of the bubble. Fig. 5 illustrates the bubble adhesion process ($d_b = 0.712$ mm) onto the hydrophobic surface in a solution of SDS. The first image at t = 0 ms illustrates the situation just before the liquid film rupture. The camera captured a bubble motion with a time step of 0.0625 milliseconds. However, images with a 0.25 millisecond time step are shown in the Fig. 5. Expansion of the TPC line is very slow and small differences are not perceived by the human eye. The bubble shape changes, particularly the oscillations in vertical direction like in pure water, were not

detected. The TPC line expansion continues together with bubble shape change, but the bubble keeps the spherical shape. The images illustrate the bubble adhesion process during the first ten milliseconds. Even after this time there are visible some small changes but the shape of the bubble does not change. The equilibrium state is reached after 50 ms. The whole sequence consists of 5400 images including final equilibrium. The bubble rising and its collision with the solid surface was not captured because the time lapse between the collision and the actual formation of the TPC line was longer than is possible to capture. Also, no bubble bouncing was observed. The extended time of the liquid interface film depletion is caused by the high concentration of surfactant molecules, which stabilises the interface film (Malysa et al., 2005).



Fig. 4. The average data of diameter of the TPC line and TPC expansion velocity in pure water for bubbles with diameters 0.70 mm and 0.85 mm. The time interval between individual points is 0.0625 ms



Fig. 5. Sequence of photos illustrating a course and outcome of the bubble ($d_b = 0.712$ mm) adhesion onto the solid surface in aqueous solution of SDS. The time interval between individual points is 0.25 ms. The final image represents equilibrium at t = 25 ms

Calculated data for this sequence, namely d_{TPC} , U_{TPC} and y_{bottom} , are given in Fig. 6. Note different time range when compared with Fig. 3. The diameter of the TPC line increases very slowly without any oscillations and the equilibrium was observed after 50 milliseconds. The bubble keeps the spherical shape and the equilibrium contact angle is 69.5°. The velocity of TPC expansion is captured in the middle image. We use the time step 0.5 ms for this calculation. The data was captured at 16000 fps but the change of d_{TPC} distance did not differ much from the calibration length. Therefore, a longer period of time was used. The chart clearly shows first the increase in U_{TPC} , where the maximum is reached after 3 millisecond. Then the velocity decreases and acquires almost unmeasurable values after 25 milliseconds. The velocity of TPC expansion in surfactant solution is at least ten times slower than in water. The last graph shows the movement of the bubble bottom apex in vertical direction. The movement of the lower part of the bubble was detected after 0.5 ms after the liquid film rupture. The bubble oscillations are completely muted during the bubble adhesion and the bottom position was stable after 12 ms.



Fig. 6. The time dependence of the diameter of the TPC line (left), TPC expansion velocity (middle) and bubble bottom apex position (right) in SDS solution for a bubble with diameter 0.712 mm

Fig. 7 shows the TPC diameter and expansion velocity for two different bubble sizes in SDS solution. The points represent the average value measured from 4-5 sequences. The TPC diameter increases with bubble size. The ratio d_{TPC}/d_b remains constant again and the average value of the contact angle is 69.4° ± 1.7°. The velocity of TPC expansion is completely different in solutions of surface active agents when compared with pure water. The velocity is much slower and we can observe an initial increase of U_{TPC} after 3 milliseconds. The times coordinate of the maximum increases with bubble size. After reaching this maximum, the velocity slowly decreases. The large scattering of data is caused by a small difference of the input data. To conclude, typical features of bubble adhesion in solutions of surface active agents are i) slow TPC line expansion (finished after 20 ms), ii) no bubble shape deformation during the adhesion, and iii) a maximum on velocity profile after 3 ms.



Fig. 7. The average data of diameter of the TPC line and TPC expansion velocity in SDS solution for bubbles with diameters 0.71 mm and 0.87 mm. The time interval between individual points is 0.25 ms

2.3. Simulations of the TPC line spreading

2.3.1 Mobile liquid/gas interface (water)

Fig. 8 presents simulation snapshots illustrating calculated outline of the bubble during (i) resting at solid surface (t < 0), rupture of the intervening liquid film (t = 0), formation of TPC hole (t = 0.1 ms) and TPC line spreading (t > 0.1 ms) for completely mobile liquid/gas interface (i.e. for situation

corresponding to distilled water). Corresponding time values are marked at each snapshot. Note, that similar to the experimental case presented in Fig. 2, also here characteristic elongation of the bubble shape, associated with the TPC formation and spreading can be noticed (see pictures for t = 0.4 and 0.7 ms). Moreover, bubble is flattened after elongation period (t = 1.2 ms), what is also consistent with experimental observations.



Fig. 8. Chosen simulation snapshots illustrating calculated bubble shapes during wetting film rupture and TPC line spreading

Evolutions of the TPC line diameter as well as the TPC line expansion velocity obtained in numerical simulations for d_b values corresponding to those studied experimentally (0.70 and 0.85 mm), are presented in Fig. 9. These dependencies look quite similar (qualitatively and quantitatively) to experimental data presented in Fig. 4, confirming quite a nice agreement between experimental observation and numerical simulation results. Characteristic peaks for the TPC expansion velocity around 1 - 2 ms after the wetting film rupture are clearly visible. Initially the velocity of TPC line spreading is comparable for both d_b values and ca. 1.5 ms first maximum for smaller bubble appears. The second maximum of U_{TPC} for larger bubble is shifted towards higher time values. Comparing the bubble shape variations observed in Fig. 8 with U_{TPC} variations presented in Fig. 9 (Fig. 2 and 4 in the case of experiment, respectively) it seems that the velocity peak is associated with the most violent bubble shape variations, i.e. with the situation, when, after the TPC formation, the bubble shape is first elongated and then flattened (the change in the bubble bottom pole position is relatively big and equal to ca. 0.2 mm). The elongation of the bubble shape results from interplay between detachment and attachment forces (Kosior and Zawala 2017). Due to the TPC formation, the capillary force (related to diameter of the TPC perimeter) is too strong for the bubble for its detachment. Consequently, the bubble is pushed back (see for example pictures for t = 1.2 - 1.3 ms in Fig. 8), what is most probable source of additional pressing force (additional pressure), facilitating (speeding up) the rate of expansion of the TPC line (maximum at U_{TPC} vs time curves).

This hypothesis impose that characteristic peaks observed at U_{TPC} vs time curves (Fig. 4 and 9) has only hydrodynamic origin and is associated with local increase of total kinetic energy of the system, resulting from quite violent bubble shape pulsations. To check correctness of this claim - thanks to the numerical simulations - we can look a little bit deeper into to the nature of this effect, analysing quantities, which are impossible to obtain experimentally. Fig. 10 presents comparison between variations in the position of bubble bottom apex (for $d_b = 0.70$ mm) and calculated kinetic energy of the system (kinetic energy of the liquid which motion is induced by the bubble shape variations). Again, *t* = 0 means rupture of the wetting film and TPC formation. As seen, initially the kinetic energy is constant and just after the moment of TPC hole formation and expansion increases significantly. Simultaneously, the bubble bottom pole approaches much closer to the solid surface – this change is quite significant and occurs in fraction of millisecond, only. Then, small changes in the y_{bottom} and the T can be noticed, followed by relatively large peak (both for y_{bottom} and T) for t equal to ca. 1.5 ms. This is exactly this same t value for which maximum at U_{TPC} vs time curve can be observed (see Fig. 4 and 9 for $d_b = 0.70$ mm). Existence of this T peak, which is a consequence of quite violent bubble shape variations (manifested by y_{bottom} changes) proofs correctness of explanation of above-mentioned mechanism and explains nature of characteristic and unexpected maxima at U_{TPC} vs time curves.



Fig. 9. Variations in: (A) diameter of the TPC line and (B) velocity of the TPC line spreading as a function of time for two different bubble sizes and mobile liquid/gas interface)



Fig. 10. Variations in position of the bubble bottom apex (solid surface positioned at y = 0) and total kinetic energy of the system during liquid film rupture (t = 0) and TPC line expansion for bubble of $d_b = 0.70$ mm (mobile liquid/gas interface)

The TPC line expansion in pure systems is influenced mainly by hydrodynamics. Such explanation is valid for smooth hydrophobic solid surface. It is possible that TPC line expansion can be influenced also by higher roughness, presence of air entrapped in the surface grooves and cavities, non-uniform chemical composition of the solid surface, different degree of hydrophobicity etc. In our system, however, we believe that hydrodynamic factor is a key parameter determining TPC line expansion course.

2.3.1 Immobilized liquid/gas interface (solution of surface-active substance)

To explain big difference between kinetics of the TPC line expansion in solution of surface-active substance and in pure water observed experimentally (see Figs. 6-7), variations in y_{bottom} of the bubble just before and after TPC hole formation was compared in Fig. 11A. To visualize strong influence of

degree of liquid/gas interface mobility, the *y*_{bottom} changes during TPC line expansion were presented there for a bubble with fully mobile (slip) and fully immobilized (no-slip) interface. As seen, fully mobile interface was much more deformable (as already discussed above) what resulted in quite violent changes in bubble bottom apex position. In contrast, due to liquid/gas interface immobilization (rigidity), which in real experimental conditions is caused by presence of surfactant and its adsorption at the bubble surface, bubble shape pulsations are significantly damped.

Certainly, as a consequence, totally different course of kinetic energy variations in the system can be observed. Due to significant attenuation of the bubble shape pulsations for immobilized liquid/gas interface, kinetic energy changes were much smaller and smoother. This explains difference in d_{TPC} and U_{TPC} evolution observed in distilled water and SDS solution determined on the basis of experimental data.



Fig. 11. Variations in: (A) position of the bubble bottom apex (solid surface positioned at y = 0) and (B) total kinetic energy of the system during liquid film rupture and TPC line expansion for bubble of two different size (mobile and immobile liquid/gas interface)

Fig. 12 presents evolution of the d_{TPC} (normalized to d_b) for mobile and immobilized bubble surface. The lack of characteristic S-shape course, already discussed in the experimental section, is clearly noticeable here for immobilized liquid/gas interface. Despite quite similar courses of expansion of the TPC line diameter determined experimentally and numerically, we were not able, unfortunately, to accurately reproduced the velocity of the TPC line spreading. Numerically determined velocity is presented in Fig. 12B (compare with Fig. 7).



Fig. 12. Time evolution of (A) normalized TPC diameter and (B) TPC line spreading velocity (numerical results)

The reason of the main (long and smooth) peak observed for surfactant solution is probably connected with the existence of the gradient of surface tension. The bubble stays under the surface for up to tens of seconds without any change or motion. During this period, the liquid thin film very slowly thins and surfactant molecules spread all over the bubble surface. After creating the TPC line we should consider also the interfacial gradient of surface tension and concentration of molecules (the reverse Marangoni flow). The bubble surface area decreases and thus the surface concentration increases. The initial increase of velocity may be related to the surface tension gradient, which was not taken into account in numerical simulations. As was already discussed, model used to mimic presence of adsorption layer at the bubble surface was simple and assumed global immobilization of the liquid/gas interface only by viscous drag increase.

3. Conclusions

The kinetics of the TPC line expansion during bubble collision and rupture at hydrophobic solid surface is significantly influenced by the bubble shape oscillations, which are diminished in case of surfactant presence.

In case of completely mobile liquid/gas interface, corresponding to pure water, characteristic bubble shape oscillations were observed during the TPC line formation and expansion. The TPC expansion velocity vs time curve exhibits a characteristic peak around 1 – 2 ms after the liquid film rupture. We proved that this characteristic peak has the hydrodynamic origin and is associated with local increase of total kinetic energy of the system, resulting from quite violent bubble shape pulsations.

In surfactant solutions, the effect of the liquid/gas interface immobilization is very significant, because the bubble shape pulsations are damped and kinetic energy changes were much smaller and smoother. The forces of surface tension gradient overcome the viscous forces and the hydrodynamic model is not able to explain the non-monotonic curve of the expansion velocity profile in surfactant solutions.

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Influence of molecular structure of alcohol-water mixtures on bubble behaviour and bubble surface mobility



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HIGHLIGHTS

- Bubble velocity in aqueous solutions of ethanol or propanol was captured using a high-speed camera.
- Drag coefficient and bubble surface mobility were evaluated.
- The molecular arrangement in the liquid influences both the bulk and interfacial properties.
- The bubble velocity and surface mobility depend strongly on alcohol concentration.

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G R A P H I C A L A B S T R A C T



ABSTRACT

The behaviour of spherical bubbles rising in water-ethanol and water-propanol mixtures was investigated experimentally for the whole range of concentrations, from pure water to pure alcohol. These two alcohols were chosen for their importance in industrial applications and for their peculiar properties resulting from the formation of organised microstructures in the non-ideal mixture at a molecular level. The effect of the composition of the alcohol-water mixtures on the physicochemical properties of the liquid was evaluated for all the solutions investigated, compared with literature values to critically access the effect of the concentration of alcohol on the bulk and interfacial properties of the mixtures. The hydrodynamic behaviour of bubbles rising in the mixtures was evaluated, by using high speed video to measure the bubble size and terminal velocity. From the corresponding drag coefficients, the mobility of the bubble's surface was determined revealing that in alcohol-water mixtures there are three regions: (1) with very low alcohol concentrations ($x_E \le 0.01$, $x_P \le 0.005$), the solutions behave as surfactant solutions with increase of bubble's drag coefficient with increase of the alcohol concentration till total immobilization of the bubble surface; (2) at intermedium concentration, the drag coefficient decreases as the concentration of alcohol increases with consequent increase of competition for location of alcohol molecules at the interface or on the bulk with formation of molecular network; (3) at high concentration $(x_E \geq 0.20 \text{ and } x_P \geq 0.07)\text{, the bubbles have again fully mobile surface as in a pure liquid.$

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1. Introduction

Gas-liquid processes are some of the most common and important operations in chemical process industry, mineral processing,

* Corresponding author. *E-mail address:* pavlina.basarova@vscht.cz (P. Basařová). and particularly biotechnology. The multiphase interaction typically occurs via the sparging of gas bubbles into a liquid media, and their subsequent rise through the bulk carrying liquid. This simple phenomenon forms the basis of several industrial multiphase processes, such as absorption, distillation, froth flotation and bubble column reactions (Kulkarni and Joshi, 2005). The equipment is hence designed and optimised using knowledge of







the fundamentals of hydrodynamics. In order to fully understand the transport processes across the interface and effectively estimate the heat and mass transfer coefficients, it is therefore essential to have a solid understanding of the bubble size and size distribution (effective interfacial contact area), dispersion, and perhaps most importantly bubble rise velocity (Ishii and Zuber, 1979). The gas phase velocity is of great importance as it determines the contact time with the liquid and ultimately the overall residence time and performance of equipment. There are a number of forces which act on the bubble during its motion that determine its surface mobility and velocity, such as buoyancy, drag, gravity, lift, surface tension, viscous forces, etc. (Magnaudet and Eames, 2000). Generalising the bubble motion for all gas-liquid systems is therefore rather complex, as these forces will vary from system to system due to their dependence upon the different bubble characteristics, physicochemical parameters and operating conditions (Kulkarni and Joshi, 2005). However, as the bubble behaviour is greatly influenced by the physicochemical properties and structure of the bulk liquid (density, viscosity, surface tension, concentration of solute, etc.), it is therefore possible to manipulate the operating regime by varying these properties (Alves et al., 2005).

The aqueous solutions of short chain alcohols, such as methanol, ethanol and propanol, are of great interest due to their atypical physicochemical properties over a broad range of composition (Dolenko et al., 2015). Given that short chain alcohol solutions are used daily in many industrial, biological and pharmaceutical processes, there is great motivation for research on these anomalies on a practical level. While the unusual behaviour has been the subject of much debate, it has been widely proven to be the result of the formation of organised, distinct local microstructures in the non-ideal mixture at a molecular level (Dixit et al., 2002). The clustering of micelle and chain-like groupings are governed by the hydrogen bonding, hydrophilic interactions and hydration between molecules (Dolenko et al., 2015). It has been welldocumented and demonstrated that the thermodynamic and transport properties of the alcohol-water binary solutions, such as volume reduction of mixture, diffusion coefficient, surface tension, heat capacity, wettability, viscosity etc., vary significantly relative to the "pure" alcohol or water states as a result (Chodzińska et al., 2012). It is therefore the aim of article to explore the consequences of the atypical properties of water-alcohol binary solutions on the behaviour of dispersed multiphase systems. To do so, the terminal velocities of spherical bubbles were determined in water-ethanol and water-propanol mixtures covering the whole range of concentration, from pure water to pure alcohols. The corresponding drag coefficients were calculated and used to assess the mobility state of the bubbles' interface. The changes in the bubble surface mobility and its dependence on alcohol concentration are discussed based on the effect of the latter on the thermodynamic properties of the solutions.

2. Theoretical part

2.1. Thermodynamic properties of alcohol-water mixtures

The aqueous solutions of simple alcohols have been thoroughly investigated for decades by biologists, chemists, and engineers due to their exceptional practical importance in many industrial, biological, and pharmaceutical applications. A clear understanding of the abnormalities in their behaviour is therefore of great importance to understand their influence on systems and for their successful application as co-surfactants and co-solvents (Chodzińska et al., 2012). The negative mixing volume is the most wellknown of the anomalies that alcohol-water solutions exhibit (Banerjee et al., 2012; Gonzalez et al., 2007; Chodzińska et al., 2012). This suggests that there are some structural changes within the binary mixture over a wide range of composition. Similarly, many experimental studies have shown that the observed entropy increase upon increasing alcohol concentration is significantly smaller than expected (Dolenko et al., 2015). This fact has been known experimentally since 1937 (Pascal and Goddard, 2012) and stimulated the theoretical investigations of Sato, who aimed to determine the origin of these abnormalities (Sato et al., 1999, 2000). According to their observations, the excess entropy S^E increases significantly when alcohol is added into water. After reaching a maximum, S^E decreases again and then it reaches a stable value which expresses the unchanging order of the molecules in the mixture. The transition concentrations are equal to 18 molar % for ethanol and 14 molar % for propanol.

Despite considerable research on these mixtures, specific details of their molecular structuring have not been realised. However, the hypothesis is it can be attributed to the better packing of alkyl-groups caused by the strengthening of the water-water hydrogen bonding network around the alcohol hydrophobic head groups. This leads to the formation of various microscopic pseudo-clathrate chainlike structures or even micelle like clusters in the surrounding water. This theory is generally supported by the majority of experts and has been independently verified by several methods over the last 20 years (Dolenko et al., 2015). D'Angelo and co-workers (D'Angelo et al., 1994) used infrared spectroscopy to study transitions in the micro-heterogeneous structures in binary alcohol/water solutions. They showed that alcohol molecules are monomolecularly dispersed and surrounded by water molecules at low concentrations. Upon increasing concentration, they observed the progressive aggregation of mixture components and a change to the hydrophobic hydration up to a critical composition maximum. Above this concentration, the water hydrogen bond network is presumed to breakdown as it subsides to the increased alcohol concentration. A similar maximum is observed using a variety of methods in this region of critical concentration. Mijakovic et al. (2011) used ultrasonic and hypersonic measurements of the speed of sound of aqueous mixtures of ethanol and found the maximum sound velocity in ethanol at $x_F \approx 0.15$, followed by a progressive diminution above this concentration. Considering sound propagates slower in ethanol, this suggested the quality of the water network is improved and more rigid with adding ethanol up to this concentration. Similar results were found by Takamuku and co-workers (Takamuku et al., 2004; Takamuku et al., 2005) who investigated the microscopic structure using the method of X-ray diffraction and mass spectroscopy. Carrying out large-angle X-ray scattering experiments, they observed a structural change from a tetrahedral-like water network to chains of hydrogen bonded alcohol molecules occurring at methanol mole fraction of $x_M \approx 0.3$, ethanol mole fraction of $x_E \approx 0.2$ and at propanol mole fraction $x_P \approx 0.1$. Above these concentrations, they showed that so-called polymer hydrates of alcohol are formed in the aqueous mixture. The mass spectroscopy indicated that the water molecules are not bonded together but rather serve as a stabiliser for the alcohol polymer clusters. A Rayleigh light scattering study of isopropanol-water binary mixtures similarly found that below a very dilute concentration ($x_{2P} < 0.05$) the isopropanol is well solvated by water molecules and individual hydrates are formed. Above this concentration, large clusters are formed in the mixture until reaching a maximum concentration of $x_{2P} \approx$ 0.30 (Wu et al., 2001). Above this concentration, the clusters are reduced to smaller aggregates. This, coupled with the similar anomalies observed with methanol and ethanol, further emphasises that this is characteristic behaviour of short chain alcohols. Differential Scanning Calorimetry had previously predicted the existence of these three distinct concentrations regions which define the solution structure and, in turn, the resulting structure

formed upon freezing methanol, ethanol and propanol (Takaizumi and Wakabayashi, 1997). At low concentrations, it was described as a water-rich region in which the water molecules completely surround the alkyl groups and undergo hydrophobic hydration. A transient region is observed within a narrow range of concentration (molar fractions $x_M = 0.3$, $x_E = 0.17$ and $x_P = 0.1$) where the number of clusters of alcohol molecules grows exponentially with increasing alcohol concentration. Outwith this region, the water behaves as a solvent in the alcohol solution as there are no longer enough water molecules to form the strong cluster networks. Additionally, Dolenko et al. (2015) presented a Raman scattering spectra of the full composition range highlighting the different strengths of hydrogen bonds. The maximum energy of hydrogen bonding was found to be higher than that of pure water at low concentrations of ethanol. The authors believed they once again confirmed the hypothesis of clathrate-like structures in waterethanol solutions. Lam et al. (2016) further confirmed these findings using X-ray absorption spectroscopy and noticed a significant enhancement of hydrogen bonding and liquid-liquid interactions upon dilution with water. The resulting improved structural ordering of the liquid was believed to provide reasonable elucidation for the negative volume and excess entropy and odd thermodynamic properties.

These findings are of particular interest to our problem as the structural changes at a molecular level within the aqueous solutions of alcohol are reflected in their physicochemical properties. This is a very important fact as alcohols can therefore be used as solvents and co-solvents to achieve desired physical properties by mixing solvents with an appropriate quantity of alcohol. The changes in the density, heat capacity and viscosity will, in turn, affect the mass and heat transfer of solutions (Chodzińska et al., 2012; Krishna et al., 2000). While the change in the density is relatively low and without extremes, the viscosity-composition dependence shows a rather substantial maximum (three times the viscosity of pure water), caused by the shortening of hydrogen bonds. Changes in viscosity directly influence the drag coefficient and velocity of rising bubbles; hence the hydrodynamics of sparged equipment will inevitably change, i.e. gas holdup and flow regimes. Independent of the benefits of their structural arrangement within the bulk liquid, the surface behaviour of alcohols is also of significant practical importance, enabling their use in conjunction with surface active agents as co-surfactants. In aqueous solutions of C1 - C8 alcohols, the changes observed in surface tension isotherm reflect the behaviour of a classical surfactant; the surface tension of alcohol-water mixture exponentially decreases with increasing alcohol concentration due to the increased concentration of alcohol molecules at the interfacial layer when compared to the bulk liquid. Chodzińska et al. (2012) carried out a comprehensive study on the surface properties of primary alcohols aqueous solutions, including the activity in the surface monolayer, surface excess concentration, and apparent and partial molar volumes. The values of the mole fraction corresponding to the aggregation of methanol, ethanol and propanol determined on the basis of the surface tension isotherms are equal to 0.28, 0.17 and 0.07, respectively. The increased alcohol concentration in the interfacial layer was proven also by Sung et al. (2005) using sum-frequency generation vibrational spectroscopy. These authors also claimed that the alcohol molecules at the surface do not have an upright orientation with a narrow distribution but instead are expected to have a broad orientational distribution alike the surface of pure alcohol.

2.2. Theory of bubble motion

Understanding and predicting the motion of bubbles in dispersed flows is a complex and ubiquitous problem in fluid mechanics. Through a trident approach of experimental, analytical and numerical work, several models for predicting bubble velocity in various multiphase systems have been proposed over the last 100 years (Kulkarni and Joshi, 2005; Magnaudet and Eames, 2000). However, these attempts to accurately predict the rise of gas bubbles in real systems have often proved less than satisfactory for a wide range of liquid phase properties and bubble sizes. The models have since been put to the test and are continually modified with the aid of more modern equipment and techniques. For example, great effort has been done to control the purity and degree of contamination of the phases in contact in multiphase systems. Additionally, the advancements in high-speed cameras, image analysis software and numerical computer simulations have enabled researchers to conclusively test the validity of many theoretical results. In practice, bubbles are typically present in multiphase systems as a swarm of dispersed bubbles of varying size. able to interact and coalesce with surrounding bubbles. Theoretically however, it is significantly more advantageous to consider the behaviour of a single bubble, which is by itself quite complex in its nature.

We will only consider the problem of the free rise of spherical bubbles in an infinite media under the influence of buoyancy. Despite the many complexities and forces which act on a bubble, the description can be simplified by considering it as the classical scenario of flow past immersed bodies and attempting a simple force balance. For the steady motion of a spherical bubble in a stagnant liquid, the drag, buoyancy and gravity forces are in equilibrium (Magnaudet and Eames, 2000):

$$\frac{1}{8}\rho_l U_b^2 C_D \pi D_b^2 = \frac{4}{3 \cdot 8} (\rho_l - \rho_g) \pi D_b^3 g \tag{1}$$

By re-arranging, we get a known relationship

$$U_b = \sqrt{\frac{4}{3} \frac{(\rho_l - \rho_g)}{\rho_l} \frac{gD_b}{C_D}}$$
(2)

Here, C_D is the drag coefficient, D_b is the bubble diameter, U_b is the terminal bubble rising velocity and ρ_l and ρ_g are the densities of the liquid and of the gas, respectively. The drag coefficient C_D is a function of the bubble Reynolds number Re_b , which is

$$Re_b = \frac{\rho_l D_b U_b}{\eta_l}.$$
(3)

Here η_1 is the viscosity of the liquid. The drag of a bubble moving at moderate Reynolds number ($Re_h \ge 1$) depends greatly on the character of the flow. The flow can be either attached to the surface of the bubble (streamlines are almost parallel to the interface) or the flow detaches from the interface (streamlines depart from the interface near equator of the bubble and a recirculating flow is present in the rear of the bubble). In the first regime, the drag is relatively low and linearly increases with the velocity. This is due to the fact that the pressure field in the rear of the bubble is similar to that across the bubble's front. Pressure forces across the top and bottom hence compensate each other, whilst the remaining drag is caused by viscosity. In the second regime, flow separates close to the bubble equator (a streamline leaves the interface at a certain angle), and there is a recirculation zone behind the bubble. The pressure field in front of and behind the bubble are very different and the pressure forces in these two parts therefore do not compensate each other. In this regime, the drag force is more important and is primarily correlated with the liquid inertia.

The first regime occurs in pure liquids when the interface is mobile. In this regime, a fluid particle close to the interface accelerates in the front part of the bubble, driven by the pressure gradient and gaining momentum. In the rear part of the bubble, the momentum allows the particle to continue motion along the interface even against increasing pressure. For these "clean bubbles", liquid therefore exerts very low shear on the bubble surface and the gas-liquid interface is mobile. Consequently, the liquid moves with low drag along the bubble surface. The expression of Mei is recommended for C_D (Mei and Adrian, 1992; Mei et al., 1994) in this regime:

$$C_{D} = \frac{16}{\text{Re}_{b}} \left(1 + \left(\frac{8}{\text{Re}_{b}} + \frac{1}{2} \left(1 + 3.315 \text{Re}_{b}^{-1/2} \right) \right)^{-1} \right).$$
(4)

The drag also depends on the presence of surface active contaminants in the system. If surface active agents are present in the liquid, they adsorb at the interface and accumulate in the rear part of the "contaminated" bubble and are not easily removed due to the high desorption energy restricting the motion in the interfacial layer. In general, fluid particles close to the interface accelerate in the front part of the bubble, driven by pressure gradient and gaining momentum. However, part of this momentum is lost due to viscous shear stress caused by the frictional forces acting on the fully or partially immobilised interface. Therefore, in the rear section of the bubble, the fluid particle does not have enough momentum to overcome the adverse pressure gradient. Fluid particles are unable to follow the interface, and separate from it. Thus the interface remains almost surfactant-free close to the front stagnation point and the resulting surface tension gradients are balanced by the shear stress exerted on bubble surface by the surrounding liquid. In contrast to clean bubbles, this shear stress is higher and the bubble drag is therefore increased. The flow around such a bubble and also its drag coefficient is well approximated by comparing the behaviour to that of a solid particle with no-slip boundary condition considered for the liquid flow (Magnaudet and Eames, 2000). Schiller and Naumann (1935) suggested the following model for predicting the drag coefficient of solid spherical particles:

$$C_D = \frac{24}{Re_b} \left(1 + 0.15 Re_b^{0.687} \right) \tag{5}$$

This relationship is also applicable for bubbles with a surface immobilised by surfactants. Turton and Levenspiel (1986) suggested similar relationship for bubbles with fully immobile surface

$$C_D = \frac{24}{Re_b} \left(1 + 0.173 Re_b^{0.657} \right) + \frac{0.413}{1 + 16300 Re_b^{-1.09}} \tag{6}$$

This relation is valid for $Re_b < 130$. For $Re_b > 130$, C_D is considered constant and equal to 0.95. It should be noted that for systems with high interfacial tension, including air/water, only a small quantity of impurities can cause significant deviations to the bubble movement and observed terminal rising velocity. This can be attributed to the elimination of internal circulation and immobilisation of the bubble surface, causing the bubble to behave anywhere between that of a solid rigid particle and clean bubble. The surfactants in the bulk phase appear to accumulate on the bubble surface due to their surface-active nature. These are then swept to the rear of the bubble due to the relative motion between the bubble and liquid phase, forming an inhomogeneous interfacial composition. Since the interfacial tension is strongly influenced by contamination concentration, the increased surfactant contamination accumulating in the rear region causes a decrease in interfacial tension. Therefore, a concentration gradient is observed between the front and rear, which must be balanced by a jump in the shear stress that opposes the counter-current flow and partially immobilises the rear surface. This phenomenon is known as the stagnant cap hypothesis and it has been generally accepted for explaining the behaviour of contaminated multiphase systems (Alves et al., 2005).

The effect of the contamination will vary greatly depending on the type and extent of contamination. An increase in contamination concentration will gradually increase the drag coefficient until a critical bulk concentration is achieved, causing the bubble to behave exactly as a rigid sphere of the same size and density. This critical concentration will vary from system to system, depending on the nature of the surfactant and bubble diameter. Additionally, as the bubble moves through the system and contaminants accumulate on the bubble, the concentration at the surface will also change with time (Dukhin et al., 2015). Given that systems operating in industry are rarely absolutely pure, typically containing contaminants such as surfactants, proteins, antifoam agents, enzymes etc., it is essential to understand their influence on the bubble characteristics in order to effectively design a multiphase system. Using the models (Eqs. (4)–(6)), it is therefore possible to predict the drag coefficient for rising bubbles in both mobile and immobile regime for a system of known physicochemical properties and bubble of known diameter. We can therefore obtain and predict the terminal rising velocity of the bubble. An understanding of the terminal velocity and bubble behaviour in a multiphase system is a useful tool for determining the residence time, gas holdup, volumetric liquid-phase mass transfer; subsequently contributing to the overall performance of the equipment. However, upon experimentally observing and determining the terminal rising bubble velocity in a system of known parameters, it is also possible to compare the findings with those predicted for both mobile and immobile surfaces to obtain a better understanding of the structural behaviour and properties of the continuous phase within the system.

3. Experimental

3.1. Alcohol-water solutions

Pure water (deionised and demineralised using a water purification system 'ULTRAPURE' produced by Millipore) was used at laboratory temperature for all measurements and in the preparation of aqueous solutions. The pH value was 6.13 and the conductivity was 1.6 μ S/cm. Pure ethanol and *n*-propanol with purities of >99.5% were supplied by Penta unless otherwise noted in the text. In these special cases the *n*-propanol with purity of >99.7% was supplied by Sigma-Aldrich. Alcohols were used as delivered without further purification. Concentrations of both ethanol-water and propanol-water mixtures expressed using molar and weight fractions are listed in Table 1 accompanied with their associated physical properties.

To prepare the aqueous alcohol solutions, water and alcohol were weighed out in appropriate amounts using a Mettler Toledo NewClassic ML balance to an accuracy of ± 0.01 g and a Mettler Toledo AE 200 balance to an accuracy of ± 0.0005 g for very dilute solutions. The solution was then stirred and shaken thoroughly to ensure complete mixing, and allowed to cool to room temperature to allow for the heat of mixing. The true molar fraction of each solution was then calculated from the mass of each component. Considering the systematic errors associated with the evaporation of components during filling and balance instrumental error, the error of this is estimated to be less than 0.1%.

3.2. Physicochemical properties

The viscosity, density and surface tension measurements were determined at 25 °C for all solutions and are listed in Table 1.

The dynamic surface tension was measured using the maximum bubble pressure method for a surface age range from 10 ms to 1 s. This measurement was performed using a Krűss Bubble Table 1

Characteristics of solutions used in the present study. Molar and mass fractions, experimental density, surface tension and dynamic viscosity at laboratory temperature.

Molar fraction	Mass fraction	Temperature (°C)	Density (kg/m ³)	Surface tension (mN/m)	Dynamic viscosity (mPa s)
x _i	Wi				
Ethanol					
0	0	25.0	997.1	72.2	0.891
0.005	0.0127	25.0	995.2	65.7	0.960
0.01	0.0252	25.2	993.4	61.7	1.020
0.02	0.0495	24.0	989.9	55.6	1.142
0.05	0.1186	24.2	979.4	45.3	1.495
0.10	0.2212	24.9	962.7	36.6	1.969
0.15	0.3110	24.9	948.6	32.3	2.214
0.20	0.3898	26.2	934.2	29.9	2.308
0.30	0.5229	25.2	904.8	27.9	2.339
0.50	0.7189	25.2	858.3	24.9	1.942
0.80	0.9106	25.2	810.3	23.0	1.386
1	1	25.0	785.6	21.8	1.099
Propanol					
0	0	25.0	997.1	72.2	0.891
0.001	0.0033	23.8	997.0	68.2	0.926
0.003	0.0099	23.8	996.0	62.3	0.962
0.005	0.0165	24.0	995.0	57.8	0.997
0.008	0.0262	23.7	993.5	52.9	1.050
0.01	0.0326	24.3	992.6	50.4	1.080
0.02	0.0638	24.5	987.7	41.9	1.257
0.05	0.1490	25.8	973.8	30.6	1.610
0.07	0.2011	26.0	963.4	28.0	1.836
0.10	0.2709	24.1	953.8	26.2	2.198
0.20	0.4552	25.0	914.2	25.3	2.608
0.30	0.5890	23.5	887.5	25.4	2.820
0.50	0.7670	23.6	850.9	24.9	2.597
0.80	0.9301	23.4	816.8	24.1	2.196
1	1	23.9	799.9	23.3	2.035

Pressure Tensiometer (BP100). We found that the surface tension is independent of the bubble age. The alcohol mixtures thus exhibit similar behaviour to pure liquids in that the dynamic surface tension is stable over time. On the liquid-air interface, the existence of a saturated monolayer with a higher alcohol concentration is presupposed when compared with the bulk (Chodzińska et al., 2012). The shortest bubble life time during the experimental measurement is 10 ms and even for this short period no change of surface tension was observed. The measurements were made at least twice and the average values of surface tension are listed in Table 1. A very clear agreement was observed when comparing the surface tension data measured with published data from multiple sources for both ethanol-water and propanol-water mixtures (Glinski et al., 1996; Chodzińska et al., 2012; Khattab et al., 2012; Vazquez et al., 1995).

The dynamic viscosity (mPa s) and density (g/cm³) were measured to an accuracy of 0.1% using a Stabinger Viscometer produced by Anton Paar (SVM3000). The rotational viscometer design is a modification of the more common Couette-type. For solutions of alcohol molar concentration <10%, the viscosity of the sample would be too close to that of pure water and viscosities obtained using the Stabinger Viscometer were no longer accurate. In this case, the viscosity was measured using a Viscoclock capillary viscometer. Each measurement was performed at least three times. We compared our experimental data with published values and an excellent agreement was observed (Gonzalez et al., 2007; Chodzińska et al., 2012; Pang et al., 2007).

3.3. Bubble velocity measurement

The experimental measurements were performed in a glass cell (30 cm height, 8 cm width and 6 cm depth) using the freely rising bubble method. Single bubbles were created by a bubble generator, produced at the top of a thin capillary (inner diameter 10 μ m, outer diameter 375 μ m) and allowed to rise through the stagnant liquid.

The bubble generator was connected to an air compressor and pressure tank to provide a constant pressurised supply of air. A computer programme was used to control the volume (and hence diameter) of each bubble by adjusting the duration of time air is filled into a capillary before the bubble is released. A capillary was lined with a hydrophobic coating to prevent the solution from entering the tip under hydrostatic pressure and, conversely, the outside surface was treated with a hydrophilic coating to ensure the bubble forms only on the tip. The programme was then initiated by the user, allowing air to flow through the valve and a bubble to form. The bubble was mechanically released from the tip by quickly moving the tip of the capillary downwards, allowing a single bubble to rise freely in the liquid. A Photron SA1.1 high speed camera with a $1024H \times 1024V$ pixel resolution, image resolution $2-3 \text{ px}/\mu\text{m}$ and Navitar macro-objective lense was used to capture monochrome images of the rising bubble at terminal velocity with a frame velocity of 2000fps. The camera was mounted on a horizontally and vertically adjustable platform, capable of precisely adjusting the position. The observed space was illuminated from behind using a Schott cold light source. The camera captured a movement of the bubble at a distance of 20 cm from the tip of the capillary. No bubble shape oscillations or acceleration were detected at this distance.

The images were focussed and calibrated before recording began. A microscopic scale printed on a glass slide was inserted vertically into the tank and carefully positioned such that the rising bubbles directly hit the bottom of the slide. The camera distance to/from the glass slide was then adjusted to focus on the printed scale and hence the rising bubbles. The frame was then saved for distance calibration in image analysis and the experiment was ready to begin. The bubble size, d_{b_i} was gradually varied between 0.4 and 1.0 mm over a total of over 50 data sets for each alcoholwater test solution. The temperature of the experiment was recorded using a mercury thermometer at the beginning and throughout the duration of the experiment to ensure the

temperature of solution remained stable. Upon finishing the tests, the tank was drained and washed thoroughly with demineralised water to avoid cross contamination between solutions. Images were evaluated using the image analysis software NIS-Elements. The bubble sequence captured was imported and adjusted to the corresponding calibration scale. The binary threshold of the images was then defined to determine an accurate and distinct boundary of the bubble. The measurement was then performed, recording the bubble diameter, x and y-position of the bubble centre and circularity of the bubble for each frame within the sequence. From the data imported, it was possible to determine the average bubble diameter for each sequence. The distance travelled by the bubble was calculated using the x and y-coordinates of the bubble centre of two consecutive shots. The terminal rising bubble velocity was calculated from dividing the distance by the time taken to travel that distance. The average value was determined from at least 20 consecutive bubble positions. We tested also the bubble sphericity. Shape of bubbles can be characterized by the aspect ratio, which is the ratio of the bubble width to height. For larger bubbles, with a diameter above 0.7 mm, the aspect ratio was 1.02. For smaller bubbles, the average value is 1.01. In pure water, the value was 1.07.

4. Results and discussion

4.1. Terminal bubble rising velocity

Fig. 1 shows the visualization of the change of terminal rising velocity (U_b) in three different solutions. The images were created by composing two frames with a time delay of 0.1 s and illustrate the distance travelled for this time period. The bubble motion is fastest in pure water (detail A) and slowest in the highly diluted solution of propanol (detail B, $x_p = 0.005$). In more concentrated solutions (detail C, $x_p = 0.07$), the rising velocity increases even though the viscosity also increases.

Data from all measurements are given in Fig. 2 (system waterethanol) and 3 (system water-propanol). Experimental data are depicted as circles; theoretical values, calculated by Eq. (2), are given as lines. The solid line (top) indicates the terminal rise velocity of bubbles with a mobile surface calculated with C_D predicted by Mei using Eq. (4). The dashed line (bottom) illustrates the predicted terminal rise velocity for bubbles with an immobilised bubble surface (C_D predicted by Turton, Eq. (6)). The values of dynamic viscosity and density listed in Table 1 were used for these calculations. The values of density and viscosity were recalculated using

Fig. 1. A composite of two images with a time shift of 0.1 s. Detail A: pure water, $D_b = 0.601$ mm; detail B: $x_P = 0.005$, $D_b = 0.607$ mm; detail C: $x_P = 0.07$, $D_b = 0.609$ mm. Light spots in the middle of bubbles are caused by light beam penetration.



the similarity model for the temperature at which the velocity measurement was done (see Table 1). The molar fraction of alcohol in solution is displayed in the top left corner of each graph.

It can be seen in all graphs that the terminal rising velocity increases with the diameter of the bubble. However, if we look at the individual graphs, we can notice differences in the manner how it increases. As expected for pure water (Fig. 2), the experimentally determined U_b shows good agreement with predictions for a bubble with mobile surface for the whole range of bubble size investigated. At concentrations below 0.01 molar fraction of ethanol, we can see that the bubble velocity is much closer to that predicted for bubbles with immobile surface and that the surface mobility increases with increasing bubble size. Similar behaviour can be observed in dilute surface-active solutions. This can be attributed to the alcohol molecules behaving as surface active contaminants and adhering onto the surface of the bubble as the bubbles rise and the surface-active molecules accumulate at the rear of





the bubble, forming a compressed adsorption layer known as the stagnant cap. This partially eliminates the internal circulation within the bubble, thereby significantly increasing the drag. According to Dukhin et al. (2015), the increase of drag coefficient is detected when the cap angle of the upper mobile top is smaller than 150°. For the cap angle smaller than 40°, the bubble behaves as a rigid sphere. The bubbles in propanol solutions with the molar fraction 0.003 and 0.005 evinced the behaviour of bubbles with completely immobile surface irrespective of the bubble size measured. Our results seem to suggest that at low concentrations, these alcohols behave as classical surfactants that accumulate at the rear of the bubble during its rise and contribute to the increase in drag force. The results also suggest that propanol is a more "efficient" surfactant as the total immobilisation was achieved for the whole range of bubble size investigated while with ethanol; only the smaller bubbles were completely immobile.

Additionally, it can be observed that in the concentration intervals, $0.02 < x_F < 0.15$ and $0.01 < x_P < 0.07$, an increase in alcohol concentration causes the bubble behaviour to tend towards Mei's predictions for a mobile surface with the values of velocity measured falling between the two limit cases. For concentrations of $x_{\rm E} > 0.15$ and $x_{\rm P} > 0.07$, the bubbles behave as if having a completely mobile interface and their velocity agrees with the prediction for C_D using Eq. (4). For all these more concentrated solutions, the existence of alcohol-water microstructures is assumed. At the interfacial layer where the alcohol concentration is higher (Chodzińska et al., 2012; Sung et al., 2005), the presence of similar microstructures is obvious. Figs. 2 and 3 also show a decreased range in the maximum diameter of the created bubble. This is a consequence of the decrease in surface tension upon increasing the concentration of alcohol in solution. The maximum size of the bubble that can be spontaneously formed from an orifice is given by capillary radius, surface tension and density difference. For our capillary, the maximum bubble diameter is therefore $D_b \approx 0.6$ mm for higher alcohol concentration.

Considering the significant abnormal variations in viscosity and density over the composition range, there are expected differences to the terminal rise velocity at a given bubble diameter. Therefore, to effectively determine the effect of increasing the molar fraction on the terminal velocity achieved, data for a single bubble diameter was used for illustration, $d_b = 0.6$ mm being chosen, as most solutions tested had data for bubbles of this size. The values were interpolated from a trend line data fit and these data is resumed in Fig. 4. As in Figs. 2 and 3, the predicted velocity limits are also shown. In Fig. 4, the influence of the structure changes is more clearly seen. Firstly, a substantial decrease in terminal rise velocity with only a small addition of alcohol is visible. At a molar fraction of 0.01 for ethanol and 0.003 for propanol, the velocity observed was almost that predicted for a bubble with fully immobile interface. As discussed before, this is due to surfactant-like behaviour of the alcohol molecules, restricting the mobility of the surface and retarding the motion of the bubble. At constant bubble size, it would be expected that with the increase the alcohol concentration, the bubble surface should remain contaminated and the bubble velocity should stay low, as typical of a rigid sphere, following the dashed line in Fig. 4. Similarly, the viscosity of these solutions increases with their concentration, having a maximum value at x \approx 0.25 both for ethanol and propanol (Chodzińska et al., 2012), so the drag coefficient is expected to increase and further retard the motion of the bubble. However, the velocity unexpectedly increases. For ethanol, this observation can be made between molar fractions of $0.05 \le x_E \le 0.10$. An even more pronounced trend was observed for propanol in the range $0.005 \le x_P \le 0.07$. Above molar concentrations of $x_{\rm E}$ = 0.15 and $x_{\rm P}$ = 0.07, the bubble velocity closely matches the predictions for a fully mobile bubble surface. This suggests that the bubble surface is now fully



Fig. 3. The bubble terminal velocity as a function of bubble diameter in propanolwater mixtures. The full line (-) represents the calculated velocity for mobile bubble surface (Eqs. (2) and (4)). The dashed line (--) represents the calculated velocity for immobile bubble surface (Eqs. (2) and (6)).

mobilised. The subsequent decrease in velocity is due to the increase in viscosity of the solution. The minimum on the velocity curve corresponds to a viscosity peak of roughly $x \approx 0.25$.

4.2. Drag coefficients

The velocity change can be emphasised further by comparing the drag coefficient calculated, by Eq. (2), for the full range of bubble sizes with their respective Reynold's number, by Eq. (3). The



Fig. 4. Terminal bubble velocity as a function of ethanol (left) and propanol (right) concentration. Data were calculated for bubble diameter 0.6 mm.



Fig. 5. Dependence of the drag coefficient on the Reynold's number of the bubble within the solutions of ethanol molar concentration. Dashed line – C_D by Eq. (6) (immobile bubble surface). Solid line – C_D by Eq. (4) (fully mobile bubble surface). Left – low x_{E_1} Right – high x_{E_2} .

results both for ethanol and propanol are illustrated in Figs. 5 and 6, respectively. In these figures, the upper (dashed) line illustrates the drag coefficient for a given Re_b predicted by Eq. (6) for an immobile bubble surface. The lower (solid) line indicates the drag coefficient for a given Re_b predicted by Eq. (4) for a fully mobile bubble surface. Here we should note that our data was also compared with other models. The Moore expression (Moore, 1963) for the mobile bubble surface is often recommended for pure liquids; but this model is suitable only for higher Reynolds numbers. In case of immobile bubbles, we obtained identical results for Schiller and Nauman model (Eq. (5)) and for Turton model (Eq. (6)). The results for the Schiller's model are not shown keep the figures clear. All the experimental data lies within the range predicted for mobile and immobile bubble surface. The data for low concentrations, with partially immobilized behaviour, are displayed in the left part of the figure, whilst the data for higher concentrations are shown in the right part.

In the case of clean water, data was in the range of Reynolds numbers between 50 and 100. Experimental drag coefficients match perfectly with predicted values for mobile surface. If alcohol is added even in trace amounts, the bubble surface mobility reduces and the drag coefficient increases, see $x_E = 0.005$ in Fig. 5 and $x_P = 0.001$ in Fig. 6. This reflects the large initial reduction in terminal velocity achieved already noticed in Fig. 4. This change occurs at very low alcohol concentrations. At these low concentrations the effect of the alcohol is felt not only in the terminal velocity of the bubbles but also on the coalescence of bubbles. Many

authors investigated the effect of alcohols on the coalescence of bubbles and it has been established that above a critical concentration, the coalescence of bubbles is suppressed. Zahradnik et al. (1999) found that the critical concentrations for ethanol and propanol are 0.178 mol/l ($x_{\rm E} \approx 0.0038$) and 0.014 mol/l ($x_{\rm P} \approx$ 0.00033) respectively - even lower than the minimum investigated here. Increasing the concentration leads to a maximum in the drag coefficient for both alcohols ($x_{\rm E}$ = 0.01 and $x_{\rm P}$ = 0.005), corresponding to the prediction for immobile interface (Eqs. (2) and (6)). After this maximum, further increasing the alcohol concentration leads to a decrease in the drag coefficient till it reaches the minimum limit for a bubble with a completely mobile surface. Both figures clearly show a transition from a bubble with an immobile surface to a fully mobilised surface upon increasing concentration. The transition point is 15 molar % for ethanol and 7 molar % for propanol. However, with further increase in alcohol concentration, there is an important change in viscosity and density of the solution which impacts the Reynold's number. Additionally, the surface tension is reduced and the bubbles formed on a capillary are smaller as a result. It is therefore difficult to compare C_D at different Reynolds numbers because there are several independent properties acting against each other. Fig. 7 illustrates the drag coefficients as a function of alcohol concentration at constant Reynolds number ($Re_b = 20$). We proposed a dimensionless function f_{CD} :

$$f_{\rm CD} = \frac{C_{D,\rm exp} - C_{D,\rm mobile}}{C_{D,\rm immobile} - C_{D,\rm mobile}},\tag{7}$$



Fig. 6. Dependence of the drag coefficient on the Reynold's number of the bubble within the solutions of propanol molar concentration. Dashed line – C_D by Eq. (6) (immobile bubble surface). Solid line – C_D by Eq. (4) (fully mobile bubble surface). Left – low x_P , Right – high x_P .



Fig. 7. Dependence of dimensionless function f_{CD} on alcohol molar fraction at $Re_b = 20$.

with $C_{D, exp}$ calculated by rearranged Eq. (2), $C_{D, mobile}$ calculated by Eq. (4) and $C_{D, immobile}$ calculated by Eq. (6). This function is 0 for bubbles with a mobile surface and 1 for bubbles with an immobile surface. The value of Re_b = 20 was chosen because we had sufficient experimental data in this area. Identical behaviour was observed at different Reynolds numbers (see Figs. 5 and 6), but results are not shown for simplicity of the figure.

It is clear from the course of both curves in Fig. 7 that ethanol and propanol in water mixtures behave similarly. Based on the alcohol concentration, we can divide these solutions into 3 distinct regions: (i) mixtures with very low alcohol content, (ii) mixtures with medium alcohol content and (iii) mixtures with high alcohol content.

In the first region, i.e. for solutions with very low alcohol concentrations, the mixtures behave as solutions containing surface active agents. Alcohol molecules that are present in the solution diffuse very quickly onto the phase interface. We can observe a significant decrease in surface tension, but the properties of the bulk liquid (density, viscosity) are still relatively consistent. The concentration of alcohol in the interface layer is higher than in bulk and thus the interface behaviour is changed. The higher concentration near the interface was confirmed both experimentally (Sung et al., 2005) and from calculations (Chodzińska et al., 2012; Yano, 2005). From the macroscopic view, we can observe the reduction of bubble velocity and the increase of drag coefficient. The alcohol molecules adsorb at the interface of the rising bubble and accumulate in the rear. Their slower and more strongly resisted desorption back to the bulk liquid causes the partial immobilisation of the interfacial layer and the resulting gradient of surface tension is balanced by shear stress exerted on the bubble surface by the surrounding liquid. When compared to 'clean' bubbles, this shear stress is higher and the bubble drag is therefore increased. The degree of surface coverage of surface-active molecules is related to the size of the bubble and is slightly reduced with increasing bubble surface area (Cuenot et al., 1997; Dukhin et al., 2015; Ramirez-Munoz et al., 2012). Therefore at constant surfactant concentration. the drag coefficient decreases and the velocity increase with increasing bubble diameter, as seen in Figs. 2 and 3. This dependence, of course, is not linear. Overall, it can be summarised that simple alcohols acting as surface active agents exhibit the maximum surface effect at very low concentrations. For propanol, we found this maximum between molar fractions of 0.001 to 0.005. For ethanol, the maximum was observed between molar fractions from 0.005 to 0.01.

In the second region, i.e. for solutions with medium alcohol concentrations, the behaviour of the mixture varies with the increasing alcohol concentration. Micro-aggregates have not begun to form, but the molecular bonds between alcohol and water are changing. For example, the structural changes were observed and described for ethanol-water mixture at concentrations between 4 and 6 molar percent (D'Angelo et al., 1994; Sato et al., 1999). Bonds are shortened and intensified and thus both dynamic viscosity and density increase. The surface tension is decreased upon increasing alcohol concentration in surface layer; this phenomenon occurs more drastically with larger hydrocarbon chains. Therefore, the surface excess of alcohol for propanol increases more rapidly than that of ethanol (Yano, 2005). Chodzińska et al. (2012) measured the alcohol surface excess concentration and differences between the alcohol activity at the solution-air interface and in the bulk phase. They found the alcohol activity maxima for propanol at concentration $x_{\rm P} \approx 0.02$ and for ethanol at concentration $x_{\rm F} \approx 0.06$. The Gibbs surface excess maximum Γ^{E} for all alcohols is the same; around 6 $\times 10^{-6}$ mol/m². After reaching this maximum, the concentration gradient reduces in conjunction with the gradient of surface tension. This surface tension gradient is balanced by the decreasing shear stress exerted on the bubble surface by the liquid. In summary, the desorption of alcohol molecules from the phase interface is facilitated which in-turn reduces the drag force and subsequently causes an increase in terminal rising velocity. This trend is especially apparent in Fig. 4. The transition to the next region is quite substantial and is related to the formation of aggregates.

The values of the mole fraction corresponding to the aggregation of ethanol and propanol determined on the basis of the surface tension isotherms are equal to 0.17 and 0.07 (Chodzińska et al., 2012). Multiple other sources have also reported a critical aggregation concentration at $x_{\rm E} \approx 0.20$ and $x_{\rm P} \approx 0.07$ (Dolenko et al., 2015). Above these concentrations, all alcohol molecules are located in clusters (or aggregates) and water behaves like a solvent in the alcohol solution (Takaizumi and Wakabayashi, 1997). Additionally, in these cases the alcohol molecules have a greater affinity to concentrate in the bulk liquid than at the interface, hence losing its' surfactant nature. The activation enthalpy and entropy suggests that the alcohol molecules in the mixture behave similarly to those in pure alcohol as the molecules form nearly the same chainlike clusters of pure components. This finding also gives evidence despite being macroscopically uniform, alcohol-water mixtures are not uniform on a microscopic to mesoscopic level (Sato et al., 1999). In the third region, i.e. for solutions with high alcohol concentrations, the properties of the investigated mixtures are most interesting. Significant variations in the solutions physical properties have already been discussed and, from an engineering perspective, the viscosity maximum is critical. Our results show that the properties of the phase interface also change significantly which affects the bubble behaviour. Upon reaching the critical aggregation concentration, the dimensionless function f_{CD} (Eq. (7)) remains constant for the remaining composition range. Put simply, the bubble surface appears to have become fully mobilised. For "mobile" bubbles, the liquid flow is attached to the bubble surface and the pressure field in the rear part of the bubble is similar to that across the bubble's front. The liquid flow thus exerts very low shear stress on the bubble surface. It can therefore be assumed that aqueous solutions of simple alcohols behave like pseudo-pure substances. The concentration of alcohol molecules in bulk liquid is too high for the formation of the surface tension gradient.

5. Conclusion

This experiment offers a means to study the previously unexplored and often misunderstood impact of the structural changes within alcohol-water mixtures across the concentration range on bubble hydrodynamics. The methods are first successfully validated by comparing the measured physicochemical properties with previously published data. It is demonstrated that the changes in internal structure and strengthening of hydrogen bonds reported in literature can significantly affect the terminal rising velocity achieved in a gas-liquid system. This report is particularly successful in differentiating the effects of changes in bubble surface mobility from the influence of known non-ideal changes in physicochemical properties on the experimental drag coefficient.

Based on the alcohol concentration we can divide the aqueous solution of simple alcohols into 3 regions: (i) mixtures with very low alcohol content, (ii) mixtures with medium alcohol content and (iii) mixtures with high alcohol content. The behaviour across the full composition range is rather complex, with a clear gradual transition between a completely immobilised bubble surface at low concentrations and a fully mobilised surface at concentrations above the critical aggregation concentration. At low concentrations ($x_{\rm E} \leq 0.01$, $x_{\rm P} \leq 0.005$), the bubble surface is immobilized. The dispersed alcohol molecules are presumed to behave as surfactants and adsorb the surface of the bubble, thus increasing the shear stress and drag. The drag coefficient is well approximated by the behaviour of a solid particle with no-slip boundary condition for the liquid flow (Schiller and Naumann, 1935; Turton and Levenspiel, 1986). In the second region, i.e. for solutions with medium alcohol concentrations, the behaviour of the mixture varies significantly with the changing alcohol concentration. Due to the changing concentration and surface tension gradients, the drag coefficient decreases. In this third region, i.e. for solutions with high alcohol concentrations, the properties of the mixtures are influenced by the existence of cluster or micro-aggregates. In this region, in which alcohol and water molecules form complete and stable clusters within the solution, due to the minimal gradient of surface tension the liquid flow exerts very low shear. For high concentrations above $x_E \ge 0.20$ and $x_P \ge 0.07$, the bubble surface is shown to be completely mobile. The drag coefficient is well approximated by the expression of Mei and Adrian (1992) and Mei et al. (1994).

Although this work does not present a model to calculate the drag coefficient and terminal velocity across the composition range, it has challenged the understanding of what influencing factors dominate the drag coefficient and resulting bubble motion in various composition regions. Thus, the work presented will be applicable from a practical and academic standpoint, and should be considered in the prediction of interfacial drag or relative velocity between phases in any dispersed two-phase system involving aqueous mixtures of simple alcohols. In future, this work will be combined with the similar ongoing study using alcohol-water mixtures with surface-active agents. Collectively, this will inevitably provide a more complete understanding of the complex inter and intra molecular mechanisms which influence bubble motion in dispersed two-phase systems.

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