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Chapter

Effect of Surfactants on Bubble-Particle Interactions

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Abstract

The interaction of air bubbles with solid particles is an important mechanism in many industrial processes, e.g., in flotation, fermentation, wetting, multiphase reactors, columns, etc. The surface-active agents are adsorbed both on air-liquid and solid-liquid interfaces and significantly influence the bubble-particle interaction. In this chapter, the mechanism, dynamics, and fundamental steps of bubble adhesion onto the solid surface are described. The first part is devoted to the description of influence of surfactants on the bubble behavior during the collision, as well as their influence on thinning and breaking of liquid film. The second part describes the effect of surfactants on the formation and expansion of the three-phase contact line between the bubble and the hydrophobic solid particle. The important role of surfactant type, concentration, and purity is discussed.

Keywords: bubble-particle interaction, surfactant, three-phase contact line expansion, phase interface, bubble adhesion, bubble surface immobilization

1. Introduction

The interaction of air bubbles with solid particles is an important mechanism in many industrial processes. Significant applications are found in the chemical and process industry (separation of coal, mineral ores, or plastics by flotation) or wastewater treatment. The multiphase flows are in general more complex due to the presence of moving boundaries separating gas and liquid phases. The degree of complexity is further increased if some surface-active agents are present in the liquid. Molecules of these substances accumulate at the interface, and they decrease the surface tension [1]. Their presence has important consequences to the flow: for example, the size distribution of bubbles or drops changes, and the rise velocity of bubbles decreases [2, 3]. The presence of surfactants in two-phase systems is very common. Sometimes, they are added intentionally to the system (e.g., in flotation as froth agents or detergents in cleaning applications). Also, many impurities in water are surface-active, and they affect flows even at trace concentrations.

In flotation, the capture of particles by rising bubbles is the central process [4]. For efficient capture between the bubble and the hydrophobic particle, they must first undergo a sufficiently close encounter. The collision process is then followed by the creation and movement of the three-phase contact line (the boundary between the solid particle surface, receding liquid phase, and advancing gas phase) until a stable wetting perimeter is established. This sequence of liquid film drainage, rupture, and contact line movement constitutes the second process of attachment. A stable particle-bubble aggregate is thus formed [5, 6].
In this chapter, the influence of surfactants on the collision and attachment process is discussed. We focused especially on (i) the influence of surfactants on bubble behavior during the collision with the hydrophobic solid particle, (ii) the drainage and rupture of thin liquid film separating the bubble and the particle, (iii) the influence of surfactants on the three-phase contact line enlargement, and (iv) the influence of different types of surfactants and their purity on bubble stability.

2. Effect of surfactants on the collision process

Before the bubble and particle collide, the bubble rises in liquid. The bubble shape and velocity follow from balance of forces acting on the bubble [7–9]. In pure liquids, the bubble surface is free of any contaminants or surfactants, and the whole bubble surface is mobile (free-slip boundary condition is valid at the bubble interface). The drag coefficient depends on Reynolds number (related to the bubble size $D_b$, bubble steady rise velocity $U_b$, liquid density $\rho$, and viscosity $\eta$) and on bubble shape defined by aspect ratio $\chi$ [8]. In the case of surfactant presence, the surfactant molecules adsorb to the bubble surface. The liquid flow around the rising bubble causes the transport of surfactant molecules resulting to the uneven surfactant distribution along the bubble surface. This leads to the formation of surface tension gradients and consequently the formation of Marangoni stresses, which reduce the mobility of a part of bubble interface [3]. Consequently, the drag coefficient increases, and the bubble velocity and distortion are reduced in comparison with clean bubbles. For high concentrated surfactant solutions, the reduction of bubble velocity is so significant that drag coefficient corresponds to the drag coefficient of solid particles with no-slip boundary condition at the interface [10].

Bubble approaching the particle surface starts to decelerate. An example of bubble-particle collision in pure liquid (deionized water) and in surfactant solution (n-octanol) is shown in Figure 1. In pure liquids, the bubble deforms from its initial shape before it collides with the solid surface [11, 12]. The deformation is caused by an increase of pressure in the liquid film separating the bubble and particle. Then, the bubble impinges on the solid. In the case of surfactant presence, the bubble deformation before the impact is suppressed. It might be expected that the presence of surfactants would affect the impact velocity of bubble hitting the surface. However, the available experimental data show that impact velocities depend on...
the Reynolds number, but the effect of surfactant presence is minor [12] even for high concentrated solutions. It has to be noted that the steady rise velocity of bubble approaching the solid is reduced in contaminated liquid, but the normalized bubble impact velocity (ratio of impact and steady rise velocity) is similar to that in pure liquid. This observation is consistent with a concept of stagnant cup model [3, 13], which assumes the free-slip boundary condition at the front of a rising bubble and no-slip boundary condition at the bubble rear. This suggests that for bubbles rising in surfactant solution, the liquid flow causes the accumulation of surfactant molecules at the rear of bubble, and the bubble front remains free of surfactants and clean.

After the impact, the bubble in pure liquid visibly rebounds from the surface (Figure 1a). In surfactant solutions, the bubble rebound from the surface is suppressed (Figure 1b) [12, 14]. While the normalized impact velocity is insensitive to surfactant presence, the rebound velocity significantly depends on the concentration of surface-active agents. Legendre et al. [11, 15, 16] introduced the concept of restitution coefficient \( \varepsilon \):

\[
\varepsilon = \frac{U_r}{U_b}
\]

defined as the ratio of rebound velocity \( U_r \) and steady rise bubble velocity \( U_b \). The restitution coefficient gives overall information about the energy dissipation during the approach, first collision, and rebound of bubble from the surface. It is observed [12] that \( \varepsilon \) decreases with increasing surfactant concentration and no rebound is observed for high concentrated surfactant solutions.

The bubble approaching the solid surface has kinetic energy which has to be dissipated before the bubble attaches to the surface. During the collision, the bubble kinetic energy is transferred to the surface energy (the bubble deforms), and/or it is dissipated by viscous stresses in thin liquid film. If bubble kinetic energy is too high to be completely dissipated in thin liquid film and during the surface deformation, the bubble rebounds from the surface. In the case of surfactant presence, the energy is dissipated also by other processes associated with adsorption/desorption of surfactant on the bubble interface, and the bubble rebound is suppressed. The possible additional energy dissipation can be caused by the increase of surface viscosity of the interface covered by surfactant and/or by Marangoni stresses around the bubble interface with uneven distribution of surfactant molecules [17, 18]. The detailed characterization of the additional energy dissipation requires the knowledge of surfactant adsorption/desorption kinetics and actual surfactant distribution along the bubble interface during its deformation. Unfortunately, this information is quite difficult to obtain under steady conditions, and it is almost impossible to obtain them under dynamic conditions. When all the bubble kinetic energy is dissipated, the bubble stops to move and to deform. However, the bubble and particle is still separated by thin liquid film, and the stable bubble-particle connection is not formed yet.

3. Wetting film drainage and rupture

For formation of a stable bubble-particle connection, the following processes have to occur: (i) thinning of the liquid layer separating the bubble and particle to a critical rupture thickness, (ii) rupture of the liquid film and formation of a “hole” at the three-phase contact, and (iii) expansion and formation of the three-phase contact line. The stability of the liquid film is commonly considered in terms of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which describes the film stability as a result of balance between long-range electrostatic interactions of the electrical double layers of two interfaces (ranging from 1 to 100 nm) and the van der Waals
interactions (1–10 nm) [19]. Above that, the properties of the solid surface (hydrophobic or hydrophilic character, roughness, heterogeneity, surface electric charge, etc.) are of crucial importance for the stability and rupture kinetics of the liquid film. During the liquid film drainage between the bubble and particle surface, the film thickness decreases with time. Depending on the solid hydrophilic or hydrophobic properties, the thin liquid film ruptures, or a stable wetting film prevents the three-phase contact formation. Generally, the more hydrophobic the surface, the less stable is the wetting film because in the case of hydrophobic particles the wetting films are generally of low stability and are expected to rupture easily and quickly [20]. The bubble attachment strongly depends also on the roughness of the hydrophobic solid surface. It was observed that the time of the TPC formation can be drastically reduced when the solid surface roughness increases [21].

3.1 Effect of surfactants on wetting film drainage and rupture

Surfactants significantly influence the dynamic properties of thin liquid films and the film lifetime. Thus, the wetting or dewetting of interface in the presence of surfactant is more complex and much less understood. It is more complex because the adsorption and orientation of a surfactant at or with respect to an interface depend on time. At the solid-liquid interface in pure liquids, we can assume a no-slip boundary condition. In contrast, 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 the excess of surfactants can cause an effective no-slip boundary condition at both interfaces (liquid-solid and liquid-air). The tangential liquid velocity at the film surfaces may be reduced by an opposing gradient of surface tension, the so-called dynamic elasticity and/or Marangoni effect. The Marangoni effect would delay the outflow of liquid and cause the dynamic contact angle to decrease. On the receding side of the TPC line, a new air-water interface is continuously created during the film drainage. Consequently, the surface tension gradients are formed because the dissolved surfactant has no time to adsorb to the interface and to establish the equilibrium between the bulk and the interface [22]. Establishing the equilibrium between the surfactant concentration in the bulk and at the interface takes a considerable time, and it is limited by the diffusion of surfactant toward the interface. The situation is even more complex because the diffusion constant depends on the amount of surfactant bound in micelles and that dissolved as individual molecules. Surfactant micelles diffuse slowly, but single molecules diffuse quickly. Thus, the equilibrium between the bulk and interface may be established faster at low concentration, where most of the surfactant is not aggregated to micelles.

Stability of the thin liquid film depends also on the electrostatic interactions, which can by either attractive or repulsive. Electrostatic component of disjoining pressure (DLVO theory) depends on electric charge of the solid surface and on the charge of the liquid-gas interface. Adsorption of the ionic surfactants at the wetting film interfaces is the main reason of the surface charge changes. As the air-water interface in clean water is negatively charged, then the electrostatic forces are repulsive for negatively charged solid surface. These interactions, typical for weakly hydrophobic surfaces, stabilize the wetting film and prevent its rupture. Opposite situation, i.e., for positively charged solid surfaces, leads to the film destabilization and to its quick rupture. It was also shown that in the case of the negatively charged solid surface the preferential adsorption of the cationic surfactant can cause destabilization of the wetting film formed by the colliding bubble [23]. The significant time reduction of the TPC formation can also be caused by the presence of air molecules, which can be either trapped in the surface irregularities or formed
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DOI: http://dx.doi.org/10.5772/intechopen.85436

spontaneously in the form of interfacial submicroscopic bubbles at rough solid surfaces. It was found that near rough hydrophobic solid surfaces, the boundary slip could be significantly increased [24–26].

4. Three-phase contact line enlargement

After the rupture of the liquid film, the liquid phase begins to retreat from the solid surface due to an uneven distribution of the liquid-gas interfacial tension. Generally, the movement of the three-phase contact line is involved in both the wetting and dewetting mechanisms. 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 force action influences the curvature of the liquid-gas interface and therefore affects the shape of the attached bubble and contact angle. The dynamic process of either wetting or dewetting can be described by the velocity of the contact line movement $U_{TPC}$ which is defined as the time derivative of three-phase contact line radius $r_{TPC}$:

$$U_{TPC} = \frac{dr_{TPC}}{dt}$$  \hspace{1cm} (2)

If we focus on the wetting process (drop spreading on the surface of the solid particle), 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 prevail during the modeling of TPC line expansion: the hydrodynamic models are rather macroscopic and disregard the role of the solid surface, whereas the molecular-kinetic models involve also the properties of solid surface.

Cox [27] established the basics of the hydrodynamic model for the wetting mechanism in pure liquids. 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 [28]. The model solves the equations governing the fluid dissipation, the continuity, and the Navier-Stokes equations and relates the expansion velocity $U_{TPC}$ to the dynamic contact angle $\theta$. The main disadvantage of this model is the inadequate description of the fluid motion very near to the contact line. The molecular-kinetic model 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 in pure liquids [29]. This model assumes the energy dissipation to occur only at the moving contact line, where adsorption and desorption processes occur. This idea is commonly applied to dynamic wetting. The movement of the three-phase contact line is ruled by the statistic kinetics of molecular events arising at the adsorption sites of the solid surface [26]. 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 [30]. A combined molecular-hydrodynamic approach is currently recommended [28, 31]. The dewetting hydrodynamics is used to describe the effect of fluid flow on the interface deformation far from the three-phase contact line. Molecular kinetics is then used for the description of dewetting process close to the contact line. A comprehensive review of wetting and spreading problematics is reported by Bonn [32], Blake [33], or De Coninck [34].
4.1 TPC line enlargement during the bubble adhesion onto the solid surface in pure liquids

Experimental studies of three-phase contact line expansion during the bubble capture on solid surface are not very often published. In pure liquids, the contact line movement is again driven by fluid dynamics, where surface, inertial, and viscous forces influence the expansion of the TPC line. Phan [30] confirmed that the combined molecular-hydrodynamic model is suitable for describing the bubble dewetting process in deionized water. However, compared to drops, the surface of the bubbles in pure liquids is much more deformable. 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 [28]. The resultant of surface, inertial, and viscous forces influences the curvature of the liquid-gas interface and therefore affects the shape of the bubble. Thus, we have to consider also additional forces resulting from quite violent bubble shape pulsations occurring during the TPC line expansion. These pulsations were confirmed both experimentally [35] and numerically [36]. A typical example is illustrated in Figure 2, where the images of a bubble having the diameter 0.7 mm are given. The TPC line expansion continues together with significant bubble shape deformation, where the bubble vertical diameter is firstly extended and then compressed. The bubble shape deformation during expansion could be described as a form of bouncing while keeping the three-phase contact line (liquid-gas interface pulsates). The elongation of the bubble shape results from interplay between detachment and attachment forces [37]. Due to the TPC formation, the capillary force is too strong and prevents bubble to detach from the solid surface. Consequently, the bubble is pushed back, which is the source of additional pressing force (additional pressure) and facilitating (speeding up) the rate of expansion of the TPC line (local maximum at \( U_{TPC} \) vs. time curves in Figure 3). Figure 3 shows the time dependence of the TPC line diameter and the expansion rate \( U_{TPC} \) defined by Eq. 2.

The rupture of a liquid film is not symmetrical with respect to the vertical axis of the bubble symmetry both for pure water and surfactant solutions. This finding is in accordance with the conclusion of Chan [38], who proved that the liquid film becomes the thinnest close to the apparent contact line. In pure water, the asymmetry of the TPC line formation leads to bubble surface oscillations and asymmetry in dynamic contact angles. Similar linear oscillations and irrotational flow during the bubble contact with the solid surface were described by Vejrazka [39].

4.2 Influence of surfactants on the three-phase contact line enlargement

In pure liquids, the stable perimeter of the TPC line is formed within a few milliseconds. The presence of surface-active agents significantly affects the kinetics of this process. The TPC line dynamics is influenced by the surfactant adhesion on
The motion dynamics of surfactant molecules toward the bubble surface should be considered as well. It can be summarized that the presence of surfactants usually slows down the entire expansion of the TPC line [43, 44]. A typical example is illustrated in Figure 4, where the images of a bubble having the diameter of 0.86 mm are given. Bubble adhesion is captured in three differently concentrated solutions of sodium dodecyl sulfate (SDS). At low concentration (detail A, solid-liquid, solid-gas, and liquid-gas interphases and also by the Marangoni flow along the bubble surface due to the changing surfactant concentration [23, 24, 37, 40, 41]. The motion dynamics of surfactant molecules toward the bubble surface [42] should be considered as well. It can be summarized that the presence of surfactants usually slows down the entire expansion of the TPC line [43, 44]. A typical example is illustrated in Figure 4, where the images of a bubble having the diameter of 0.86 mm are given. Bubble adhesion is captured in three differently concentrated solutions of sodium dodecyl sulfate (SDS). At low concentration (detail A,
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\[ c = 5 \times 10^{-5} \text{ mol/l}, \]

the higher mobility and viscoelasticity of the bubble surface, which is manifested by shape oscillations, can be seen. The expansion of TPC line is quick; the equilibrium is reached in 15 ms. At highest concentration (detail C, \( c = 2 \times 10^{-2} \text{ mol/l} \)), the mobility and viscoelasticity of the bubble surface are low, and all oscillations are damped. The bubble does not lose its spherical shape. The expansion of TPC line is slower; the equilibrium is reached in more than 40 ms. As the surfactant concentration increases, the wetting angle decreases. Detailed sequences are published in [35].

Figure 5 shows the time dependence of TPC line expansion velocity for SDS solutions used in Figure 4. Compared to bubble adhesion in water (\( U_{\text{TPCmax}} = 0.48 \text{ m/s} \)), adhesion of bubbles in surfactant solutions is significantly slowed down, and \( U_{\text{TPCmax}} \) ranges from 0.15 m/s (low SDS concentration) to 0.03 m/s (high SDS concentration). In the case of the highest SDS concentration, the critical micellar concentration is exceeded, and the TPC expansion velocity is very slow.

The nonlinearity of expansion velocity was also observed which cannot be explained by molecular-kinetic or by hydrodynamic model. Immediately after the TPC line formation, the solid-liquid and the air-liquid interfaces merge. 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 electrostatic double-layer repulsion. This long-range repulsion would keep the interfaces apart and delay the dewetting on the receding side [30]. Thus, the resulting gradient in surface tension would slow down the drainage of the liquid film and extend the bubble adhesion time. The dependence of the dynamic wetting angle on the dynamics of the three-phase interface motion has been confirmed experimentally in other cases as well [45].

5. Influence of different types of surfactants and their purity on bubble stability

The adhesion of the bubbles is significantly influenced by the type, charge, length, and purity of the surfactant, pH, or other additives such as salts. The effect
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DOI: http://dx.doi.org/10.5772/intechopen.85436

of nonionic, anionic, and cationic surfactants on kinetics of the TPC formation is completely dissimilar for hydrophobic and hydrophilic solid surfaces. The following surfactant types can be considered: (i) ionic surfactants on hydrophobic (nonpolar) surfaces, (ii) ionic surfactants on hydrophilic (polar) surfaces, (iii) nonionic surfactants on hydrophobic surfaces, and (iv) nonionic surfactants on hydrophilic (polar) surfaces [46]. In the case of the hydrophobic surfaces, the charge of surfactant plays a minor role [46], and the TPC line is formed and enlarged always, independently on the surfactant type [23]. On hydrophilic surfaces, the TPC line dynamics is electrostatically driven, and thus, the bubble attachment is determined by charge and/or polar interaction [46]. For example, the bubble attaches to negatively charged surface only when the natural negative electric charge at the bubble surface is reversed to positive, which can occur only in cationic surfactant solutions [23].

An important factor is also the molecular structure of the surfactant. The most common nonionic surfactants are those based on ethylene oxide. They are produced by ethoxylation of a fatty chain alcohol, and the most common ones have 12 carbons in the alkyl chain. In the case of large or other complex molecules, one should expect an adsorption barrier that consists of these branched molecules captured on phase interface and that prevents the adhesion of other molecules [47]. 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. The transport of such molecules is low, and thus, surprisingly, their influence on the velocity of TPC line expansion could be very low [44].

The ionic surfactants used both in industrial applications and in scientific studies contain some admixtures of nonionic surfactants or other contaminants. The principal organic contaminants are homologous alkyl sulfates, n-alcohols, and carboxylic acids. Dodecanol is the most important contaminant and is one of the hardest to remove [48, 49]. 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 [50, 51], shear viscosity, and foam stability [50, 52]. Impurities (contaminants) usually act as cosurfactants or mixtures of two different types of surfactants. Mixed surfactants exhibit synergism which means that their interfacial properties are more pronounced than those of the individual components themselves. A significant reduction in surface tension is typical. Therefore, the contaminants decrease the ability of bubbles to attach to solid surfaces when compared with the mono-surfactant solution. The influence of

Figure 6.
Images of bubbles captured on the hydrophobic surface in water, in aqueous solutions of SDS (sodium dodecyl sulfate), and in E₁₂O₅ (pentaethylene glycol monododecyl ether). θ and γ denote the contact angle in liquid phase and the surface tension, respectively.
contaminants is crucial below the critical micelle concentration of the main surfactant, and it may even happen that the capture of bubbles is avoided [43]. Typical example, images of bubbles in five different solutions, is illustrated in Figure 6. The bubble is most stable attached in clean water. In solutions of common surfactants, e.g., in SDS, the wetting angle and thus the bubble stability decrease with the decreasing surface tension of the solution. For molecules with complex structure or, in the case of contaminants or additives, this simple rule may not apply.

6. Conclusions

In this chapter, we have reported on the state-of-the-art research on the influence of surface-active agents on bubble-particle interactions during the flotation process. The surfactants adsorb onto the phase interface and change its properties. Upon adhesion to the liquid-gas interface, surfactants reduce the mobility of the bubbles, which reduces their rising velocity and suppresses the shape oscillations. The surfactants also prevent the thinning of the liquid film, leading to an undesirable prolongation of the time required to break the film, and create a three-phase contact. The surfactants further extend the three-phase line extension and reduce the resulting bubble stability.

Acknowledgements

The authors would like to acknowledge the financial support from the specific university research fund of the Ministry of Education, Youth and Sport of the Czech Republic No. 21-SVV/2018.
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