



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



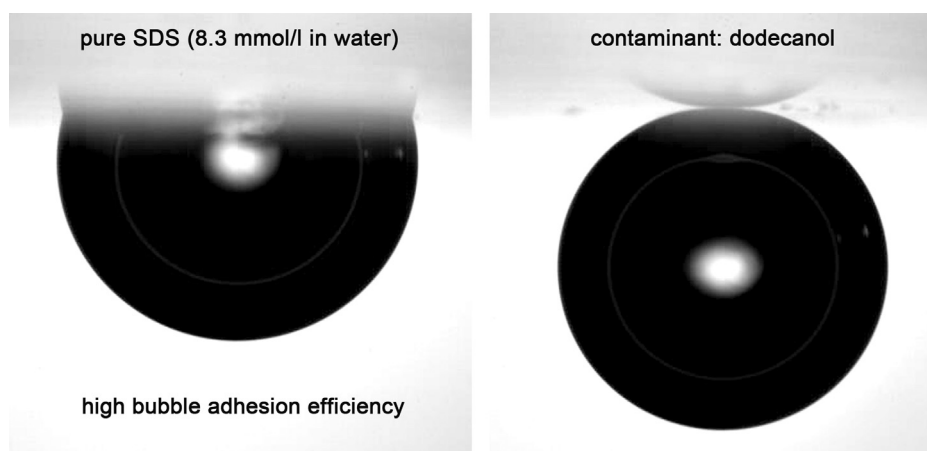
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HIGHLIGHTS

- 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 wettability is studied.
- The significant influence of contaminants even in trace concentration is discussed.

GRAPHICAL ABSTRACT



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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

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, carboxy-

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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 oil-water 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].

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