



Influence of non-ionic and ionic surfactants on kinetics of the bubble attachment to hydrophilic and hydrophobic solids



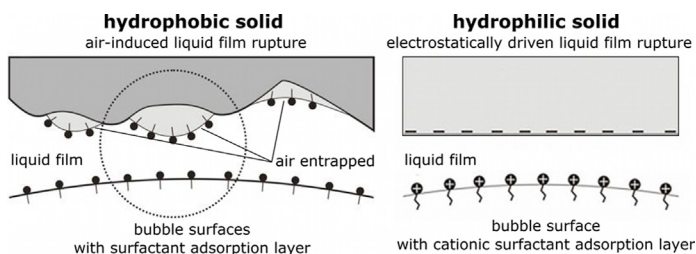
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HIGHLIGHTS

- At hydrophobic solid the TPC is formed independently on the solution composition.
- Time of the TPC formation is prolonged at higher surfactants concentrations.
- The TPC formation at hydrophobic solid surface is air-induced.
- At hydrophilic solid the TPC formation depends on the surfactant polar group type.
- For hydrophilic solid surface the TPC formation is electrostatically driven.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 October 2014

Received in revised form

21 November 2014

Accepted 23 November 2014

Available online 29 November 2014

Keywords:

Surfactant

Liquid film

Bubble attachment

Three-phase contact

Nano-bubble

Electrostatic interactions

ABSTRACT

The paper is devoted to kinetics and mechanism of the three-phase contact (TPC) formation by the colliding bubble at model hydrophobic (polytetrafluoroethylene – Teflon) and hydrophilic (muscovite mica) solid surfaces. To determine influence of type of the surfactant polar group the experiments were carried out in solutions of non-ionic (n-hexanol and n-octanol), cationic (n-octyl-(OTABr), n-dodecyl-(DDTABr) and n-hexadecyl-trimethylammonium (CTABr) bromides, and anionic (sodium hexadecyl sulfate (SHS)) surface active substances (SAS). The time of the TPC formation (t_{TPC}) and timescale of rupture of the thin liquid film separating the colliding bubble and a solid surface was determined using high-speed video registrations. The t_{TPC} was defined as the time span from the moment of the bubble first collision up to the liquid film rupture and formation of the TPC (dewetted) hole. It was shown that the influence of SAS on the kinetics of the TPC formation could be completely different depending on the hydrophilic/hydrophobic properties of the solid surface. At the Teflon surface the TPC was formed always, both in distilled water and in SAS solutions of various composition and concentration. Moreover, the t_{TPC} was significantly prolonged at higher SAS concentrations, independently on the SAS type (ionic, non-ionic). At the mica surface the wetting film was stable and the TPC was never registered in distilled water as well as in solutions of non-ionic and anionic surfactants. However, the TPC was formed at the mica surface in solutions of cationic surfactants, but the t_{TPC} values were decreasing with increasing cationic surfactants concentration. Mechanism of the TPC formation is presented and reasons of the completely different influence of SAS on kinetics of the TPC formation at the hydrophilic and hydrophobic solid surfaces are explained.

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1. Introduction

Kinetics of the three-phase contact (TPC) formation at solid surfaces of different hydrophobicity is strongly affected by stability of the wetting films formed. Generally, the more hydrophobic the surface, the less stable is the wetting film [1,2]. Depending on the solid hydrophilic/hydrophobic properties, the thin liquid film (TLF), separating the colliding bubble from the solid surface in pure water, either (i) ruptures [3], or (ii) a stable wetting film prevents the three-phase contact formation [4,5]. Roughness is another important feature of the solid surface affecting stability of the wetting films. The solid surfaces of the same chemical and physical properties but of different roughness show different wetting behaviors. It is well known that increase of the surface roughness causes increase of the contact angle [6–10]. Anfruns and Kitchener [11] showed that flotation efficiency of highly hydrophobic (via surface methylation) spherical glass and irregular quartz grains was much greater in the case of irregular (rough) quartz grains. Similar results were obtained in studies on influence of the solid surface roughness on time of the TPC formation and the bubble attachment, carried out for the model system where a rising bubble collided with hydrophobic (Teflon) plate [3,12] – greater surface roughness caused shortening the bubble attachment time. Krasowska et al. [3,13] attributed this correlation to: (i) the radius of the local liquid film formed at irregularities of the solid surface of different roughness, and (ii) the presence of air entrapped in the surface scratches, grooves and irregularities (more air can be entrapped at rougher surface). Presence of air at hydrophobic surface (nano- and/or micro-bubbles) means also that locally there are formed the foam films between the micro- and/or nano-bubbles attached to the Teflon surface and the colliding macro-bubble. The air presence affects stability of the thin liquid films (TLFs) formed [14–18], is crucial for superhydrophobicity [19], can lead to changes in hydrodynamic boundary slip conditions [20,21], and can affect kinetics of technological processes, e.g. flotation [3,12,22–25].

In flotation the hydrophilic/hydrophobic properties of the ore components are modified via a proper choice of chemical reagents, called collectors. The collectors are added to adsorb selectively on surfaces of grains of the useful ore component and increase their hydrophobicity [26]. Frothers are the surface active substances used in flotation for a larger gas dispersion (smaller bubbles) and to assure formation of a froth layer of a desirable stability [26–28]. They should also facilitate the three-phase contact formation [27,29] and prevent coalescence of the bubbles formed in the flotation cell [30,31]. However, too high frother concentrations can be counterproductive for flotation effectiveness. As showed recently [12], the time of the bubble attachment to hydrophobic solid surfaces of different roughness can be prolonged significantly at high concentrations of surface-active substances (SAS). This rather unexpected effect of prolongation of the TPC formation time (t_{TPC}) at high SAS concentrations was attributed to air presence at hydrophobic surfaces [12,13,32]. When air is entrapped in irregularities of hydrophobic surface then foam films are formed locally between the micro- and/or nano-bubbles and the colliding macro-bubble. Higher stability of the foam films at high SAS concentrations caused the t_{TPC} prolongation.

In the case of the hydrophilic solids there is no air entrapped at such surfaces (no nanobubbles) and therefore the thin liquid film, formed between colliding bubble and solid surface, is a typical wetting film. Stability of the thin liquid film depends on the electrostatic interactions, which can be 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 [33–35]. As the air/water (clean water) interface

is negatively charged [36–39], then for negatively charged solid surface the electrostatic forces are repulsive. These interactions, for weakly hydrophobic surfaces, stabilize the wetting film. Opposite situation, i.e. positively charged solid surface, leads to the film destabilization and its rupturing [39–41]. It was also showed [42,43] that in the case of the negatively charged solid surface the preferential adsorption of the cationic surfactant at the liquid/gas interface can cause destabilization of the wetting film formed by the colliding bubble. It needs to be underlined here that cationic surfactants can also adsorb on the negatively charged solid surface. This means that, at high solution concentrations, can also cause reversal of the solid surface charge, what can lead to obtaining the stable wetting films [33,34,44]. The strength and range of interactions of these electrostatic forces can be modified via variations of the solution pH and electrolyte concentration, especially in the case of hydrophilic and weakly hydrophobic surfaces [5,32,45,46].

The paper presents results on influence of different surfactant types on kinetics of the three phase contact (TPC) formation on model hydrophilic and hydrophobic solid surfaces. Experiments were carried out in solutions of n-hexanol, n-octanol, n-octyltrimethylammonium (OTABr), n-dodecyltrimethylammonium (DDTABr), n-hexadecyltrimethylammonium (CTABr) bromides and sodium hexadecyl sulfate (SHS). Non-ionic, cationic and anionic surfactants were used to determine influence of the surfactant polar group on stability of the liquid films formed at the solids surfaces by the colliding bubble. The time of TPC formation and time of drainage of the TLF at the mica and Teflon surfaces were determined. Mechanism of the TPC formation at hydrophilic and hydrophobic solid surfaces in presence of different surfactants is described.

2. Experimental

2.1. Methods

Single bubbles were formed at the capillary orifice at the bottom of a square borosilicate glass column (50 mm × 50 mm). The horizontally positioned solid surfaces (mica or Teflon plates) were located at the distance $L = 3$ mm from the capillary orifice, beneath the solution surface. The equivalent diameter of the bubble (d_{eq}) detaching from the capillary of the inner diameter of 0.075 mm was 1.48 ± 0.03 mm in distilled water. A high-speed camera (SpeedCam MacroVis, 1040 frames per second) was used to monitor and record the bubble approach and collisions with solid surfaces. Each experiment was repeated 20–40 times to get reliable data. More details about the experimental set-up and procedures can be found in our previous papers [3,47].

The advancing contact angles were determined from the sessile drop shape analysis (Kruss DSA100 apparatus). A single drop of liquid (volume ca. 5 μL) was deposited at the solid surface and the values of the contact angle were determined using KRUS Software for Drop Shape Analysis DSA3 by tangent method, i.e. fitting of polynomial function at the contact point where the liquid and the solid intersect.

2.2. Materials

N-hexanol and n-octanol were the non-ionic surface-active substances (SAS), n-octyltrimethylammonium (OTABr), n-dodecyltrimethylammonium (DDTABr) and n-hexadecyltrimethylammonium (CTABr) bromides were the cationic surfactants, and sodium hexadecyl sulfate (SHS) was the anionic surfactant used. All reagents were commercially available products of the highest available purity: n-hexanol, Sigma $\geq 99\%$; n-octanol, Sigma $\geq 99\%$; OTABr, DDTABr, CTABr, Sigma $\geq 98\%$;

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