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Influence of dynamic adsorption layer formation on bubble attachment to quartz and mica surfaces in solutions of pure and mixed surface-active substances

Agata Wiertel-Pochopien, Jan Zawala

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland

Corresponding author: nczawala@cyfronet.pl (Jan Zawala)

Abstract: The paper presents systematic studies on influence of state of dynamic adsorption layer (DAL) induced at the rising bubble interface on time-scale of the bubble attachment to quartz and mica surfaces immersed in pure n-cetyl-trimethylammonium bromide (CTAB) and mixed octanol/CTAB solutions of different concentrations. It was found that in the case of pure CTAB solutions, the influence of the DAL on time of bubble attachment and the three-phase contact (TPC) formation (t_{TPC}) strongly depends on solution concentration. Generally, two solution concentration regimes were distinguished – low and high - for which different degree of solid surfaces hydrophobization was observed. It was determined that for low concentration regime the solid surface is only slightly hydrophobized while for high regime, hydrophobicity of the solid surface is much higher. Consequently, wetting film rupture for low concentration regime is governed by electrostatic interactions while for high concentration regime significance of these interactions is much smaller. As a result, the DAL influenced the film rupture in these two regimes in a quite different manner. For mixed n-octanol/CTAB solutions it was found that CTAB molecules presence is necessary condition for wetting film destabilization. Moreover, thanks to the developed approach, allowing control of initial adsorption coverage over the bubble surface (independently on concentration), it was proved that constant adsorption degree of CTAB molecules at the bubble surface in the mixture, leads to identical times of the TPC formation.

Keywords: bubble, dynamic adsorption layer, wetting film, quartz, mica, three-phase contact

1. Introduction

Kinetics of a bubble collision and the three-phase contact (TPC) formation at solid surface is very important in many different processes involving multiphase flows, especially separating process, for example froth flotation. Froth flotation is a physicochemical separation technique used worldwide on a great scale to enrich ores of valuable minerals. It is based on the selective gas bubbles attachment to the hydrophobic surface of minerals being separated from the gangue. Collision of the bubble with a surface of solid material can be considered as one of the most crucial and fundamental acts of flotation separation process. During an air bubble collision with a solid surface the wetting film is formed i.e. liquid layer separating gas/liquid and liquid/solid interfaces. Three-phase contact is formed when a wetting film ruptures, which is usually the case for sufficiently hydrophobic surfaces. One of the most important factors influencing kinetics of the TPC formation, which influences also stability of wetting films, is the dynamic adsorption layer (DAL) formation over the rising bubble surface (Zawala et al., 2015; Niecikowska et al., 2010). Formation of the DAL means an establishment of motion induced uneven distribution of adsorption coverage over a moving bubble interface (Dukhin et al., 1995). The kinetics of the DAL formation in surface-active substances (SAS) solutions depends on concentration and initial adsorption coverage at the rising bubble surface (Dukhin et al., 2015; Kosior and Zawala, 2018). The DAL formation causes the minimum adsorption coverage at the bubble upper (top) surface

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(Γ_{top}) and the maximum one at the rear surface (Γ_{rear}), i.e. $\Gamma_{top} < \Gamma_{eq} < \Gamma_{rear}$, where Γ_{eq} is the equilibrium surface concentration over the motionless bubble. This difference in adsorption coverage causes lower velocity of the rising bubble as a result of appearance of the surface tension gradients opposing shear flow, leading to partial or full immobilization of the gas/liquid interface and increase resistance (drag) force. Development of full DAL structure at the rising bubble is time dependent and concentration dependent (depends on surfactant type and concentration as well as distance covered by the bubble from its formation point). Monitoring of the bubble motion parameters provides very useful information about the stages of the DAL formation. Establishment of a bubble terminal velocity means that the DAL is fully formed and a gas/liquid interface is fully immobilized.

As was mentioned above, the TPC is formed when draining liquid (wetting) film reaches its critical thickness and ruptures. For hydrophilic solid surfaces the thin wetting films stability depends mainly on electrostatic interactions between interfaces creating the film (Stockelhuber, 2003; Zawala et al., 2015). Depending on electrical surface charge bearing by liquid film interfaces, such interactions can be attractive and cause film rupture or repulsive, stabilizing the system. In the case of quartz and mica surfaces immersed into aqueous phase, the liquid/solid interfaces are negatively charged practically in the whole pH range, similarly to liquid/gas (bubble) surface (Zembala and Adamczyk, 1999; Yang et al. 2001; Kowalczuk et al. 2016; Fa et al. 2005). Therefore, during bubble collision with quartz or mica surface in water, repulsive interactions cause that wetting film is stable. In the case of quartz, repulsive interactions, stabilizing aqueous liquid film are dominant even though quartz is naturally, weakly hydrophobic mineral (Kowalczuk and Drzymala, 2016) with contact angle of water ranging between 20-30° (Zdziennicka et al., 2010; Kowalczuk, 2015; Kowalczuk et al., 2016). Liquid film stability is the main reason of lack of quartz flotation in pure water system (Kowalczuk and Drzymala, 2016). Addition of cationic surfactant can reverse the surface charge both at liquid/gas and/or liquid/solid interfaces. For example, in the case of cationic n-cetyl-trimethylammonium bromide (CTAB), depending on solution concentration, the CTAB molecules can preferentially adsorb at bubble surface (and act as flotation frother) or can also adsorb at solid surface (and act simultaneously as a frother and collector). According to the literature, point of zero charge of the bubble interface in CTAB solution is at $c_{CTAB} \approx 1\times10^{-7}$ M (Graciaa et al., 2006), therefore rupture of the wetting film and the TPC formation at quartz is expected for higher CTAB concentrations, where the bubble surface is positively charged as a result of CTAB molecules adsorption. From the other hand, charge reversal of the quartz surface in CTAB solution (from negative to positive) occurs for $c_{CTAB} \approx 6\times10^{-5}$ M (Churaev et al., 2000), so in higher CTAB concentrations one can expect electrostatic repulsion between positively charged bubble and quartz surface within a liquid film. Similar situation is expected for mica surface, for which point of zeta reversal was determined to vary from $c_{CTAB} = 2\times10^{-5}$ M (Fa et al., 2005) to 6×10^{-5} M (Pashley, 1985).

In this paper, we present results of the experimental studies on effect of state of dynamic adsorption layer on kinetics of a single bubble attachment to quartz and mica surfaces in pure and mixed solutions of n-octanol and CTAB of various concentration. Experimental results, partially presented in our previous paper (Zawala et al. 2017), were supplemented by experimental data on kinetics of the bubble attachment to solid surfaces located at different distances from the bubble formation point. The significant effect of the DAL presence on time-scale of a bubble attachment is presented. Moreover, we show that importance of electrostatic interactions diminishes with increasing hydrophobicity of the solid substrate.

2. Materials and methods

2.1. Materials

High purity (>98% SiO_2) natural piece of quartz (mono-crystal of surface dimensions ca. 20×10 mm) and pieces of muscovite mica (Continental Trade Sp. z o.o.) were used in contact angle measurements and experiments on kinetics of the TPC formation by the colliding bubble.

N-cetyltrimethylammonium bromide (CTAB - Sigma Aldrich), and n-octanol (Merck) used in the experiments were commercial reagents of highest available purity (≥99%). Mucasol®, a commercially available cleaning liquid, was purchased from Sigma Aldrich. Milli-Q® water was used for preparation of solutions of cationic and non-ionic surface-active substances and their mixtures.

Composition of mixed n-octanol/CTAB solutions were identical to that used in our previous studies (Zawala et al., 2017), where synergetic effect of non-ionic n-octanol and cationic CTAB mixtures for quartz particles flotation response was studied and discussed. Briefly, the n-octanol/CTAB mixtures were prepared by dilution of certain amount of n-octanol solution of concentration 1×10^{-3} M with CTAB solution of concentration 5×10^{-7} M. The mixture composition was expressed as volume fraction of n-octanol solution. For example, to prepare the mixture, where volume fraction of n-octanol solution was equal 20%, 200 cm^3 of n-octanol of concentration 1×10^{-3} M were mixed with 800 cm^3 of CTAB solution of concentration 5×10^{-7} M. Such procedure was related to change in both the n-octanol and CTAB initial concentrations, which final values are listed in Table 1.

Table 1. Concentration of n-octanol and CTAB in their mixtures used in the experiments

volume fraction of 1×10^{-3} M n-octanol solution [%]	**$V_{octanol}$ (1×10^{-3} M)** [cm^3]	**V_{CTAB} (5×10^{-7} M)** [cm^3]	**$c_{octanol}$ in the mixture** [M]	**c_{CTAB} in the mixture** [M]
0	0	1000	0	5.0×10^{-7}
1	10	990	1.0×10^{-5}	4.95×10^{-7}
5	50	950	5.0×10^{-5}	4.75×10^{-7}
10	100	900	1.0×10^{-4}	4.50×10^{-7}
17.5	175	825	1.75×10^{-4}	4.10×10^{-7}
25	250	750	2.5×10^{-4}	3.75×10^{-7}
35	350	650	3.5×10^{-4}	3.25×10^{-7}
50	500	500	5.0×10^{-4}	2.50×10^{-7}

2.2. Contact angle determination

Apparent contact angle (θ) of solid substrates was measured using Kruss DSA100 apparatus, by sessile drop technique. Dry solid samples were placed in the closed glass chamber filled partially with small amount of the liquid used for the contact angle measurements for equilibrium saturation of the gas phase with the liquid vapour. A single drop of cationic surfactant solutions of various concentrations (volume ca. 5 μl) was deposited onto the solid surface and the variations in advancing contact angle with time were measured using circle fit method. Each experiment was repeated at least 5 times at different locations of the dry solid surface. Final value of the apparent contact angle was calculated as an average, for the time period, when the θ was no longer varied. The quartz surface was carefully washed after each series of the measurements (each concentration of the solution studied), using diluted Mucasol® and large amount of Milli-Q® water. Afterwards, the quartz surface was dried under a jet of compressed and filtered air. For mica, every series of experiments were performed using freshly cleaved surface.

2.3. Experimental set-up

Schematic illustration of the experimental set-up used in our experiments is presented in Fig. 1. It consists of square glass column with glass capillary at the bottom, high-speed camera for observations and recording of dynamic phenomena occurring during bubble collision, formation of the wetting films and bubble attachment to the solid substrates and precise system of gas dosage. The recorded movies were analyzed frame-by-frame to determine time of the three-phase contact (TPC) formation (t_{TPC}), i.e. time interval between bubble first impact with solid surface and wetting film rupture. This time period is composed of time of the bubble bouncing (t_b) and time of drainage of a liquid film to its critical thickness of rupture (t_d). The system for single bubble generation used in our previous studies (Kosior et al. 2014, Zawala et al. 2017) was modified. Single bubbles were formed at the capillary orifice with use of bubble generator (Zawala and Niecikowska 2017), based on precise control of pressure in the system, allowing precise adjustment of the bubble detaching interval. Moreover, the adsorption time controlling device, i.e. "bubble trap", which was also developed in our laboratory, was applied in some of experiments. This trap schematic illustration, as a part of the whole set-up, can be seen in Fig. 1A, while Fig. 1B presents its photograph. The bubble trap was based on programmable stepper motor and bubble holder (glass dome) located just above the capillary orifice. The moment of trap closure and opening (full dome rotation around its own axis) was controlled and synchronized with moment of generation of a single bubble. It was therefore possible to control precisely the time of bubble residue inside the trap, i.e. control of time available for adsorption of surface-active molecules at the bubble (liquid/gas) surface (control of initial adsorption coverage). In order to investigate influence of state of adsorption layer over the colliding bubble surface on stability of wetting films formed at studied liquid/solid interface, the solid substrates were mounted at three different locations from the bubble formation point (L), namely: "close", for which $L = 3$ mm, "moderate" where $L = 25$ mm and "far" where $L = 150$ mm. The "moderate" distance applied was a consequence of "bubble trap" dimensions – for experiments without the trap the $L = 3$ mm, otherwise L had to be a little bit longer to keep the trap beneath the solid surface immersed into the aqueous phase.

Prior to each experiment quartz and all glass parts of the experimental set-up were carefully washed in diluted Mucasol®, and then rinsed with large amount of Milli-Q® water. Fresh and clean mica surface was prepared by removing (cleaving) two outside layers. The experiments were carried out at room temperature (22°C).

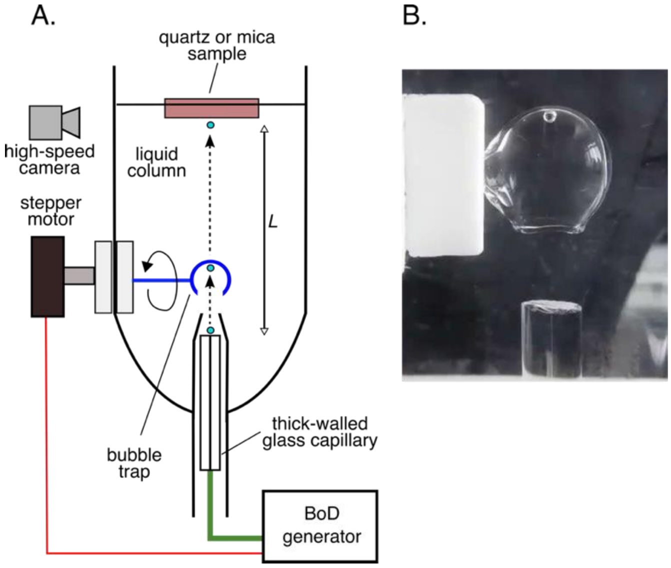

Fig. 1. Experimental set-up

3. Results and discussion

3.1. Single-component CTAB solutions

Fig. 2 presents values of apparent advancing contact angle (θ) measured using sessile drop technique at quartz and mica surfaces, as a function of CTAB concentration. It can be seen that variations in the contact angle values of quartz and mica take place at different CTAB concentration ranges. In the case of quartz, for low CTAB concentrations ($c_{CTAB} < 2\times10^{-6}$ M) the θ is practically constant and corresponds to the value measured for pure water, i.e. 28° ± 6° (Zdziennicka et al., 2010; Kowalczuk et al., 2016). Significant increase in θ can be observed for $c_{CTAB} > 3\times10^{-6}$ M and is caused by CTAB molecules adsorption at solid surface (Churaev et al., 2000; Zdziennicka et al., 2009; Starov, 2010). For mica surface, both in water and low c_{CTAB} values ($c_{CTAB} < 1\times10^{-5}$ M) complete spreading of the liquid droplet was observed during experiments. In this CTAB concentration range adsorption of surfactant molecules do not affect the solid surface hydrophobicity. It was possible to determine the θ values starting from $c_{CTAB} = 1\times10^{-5}$ M ($\theta = 23.4 \pm 14°$). Relatively high standard deviation for this θ value of CTAB concentration indicates inhomogeneity of the mica surface in respect to the CTAB molecules adsorption.

As seen in Fig. 2, there were also differences in the maximum contact angle values (θ_{max}) for both minerals, despite the fact that θ_{max} was observed at similar CTAB concentration equal to ca. 1×10^{-4} M.

For mica, the θ_{max} was equal to 82.7 ± 1.1° while for quartz it was smaller and equal to 50.8 ± 1.4°. These values correspond well to the literature data where similar θ_{max} was determined for quartz (Starov, 2010; Zdziennicka et al., 2010) and mica (Eriksson et al., 1996) surfaces. Moreover, increase in the mica contact angle corresponds well to the point of zeta reversal (PZR) in CTAB solutions, reported to be equal 2×10^{-5} M (Fa et al., 2005). After maximum value, decrease in the contact angle can be observed for both mineral surfaces, what is a consequence of formation of bilayer structure of adsorbed CTAB molecules and hydrophilization of the solid surfaces (Eriksson et al., 1996; Churaev et al., 2000; Zdziennicka et al., 2010).

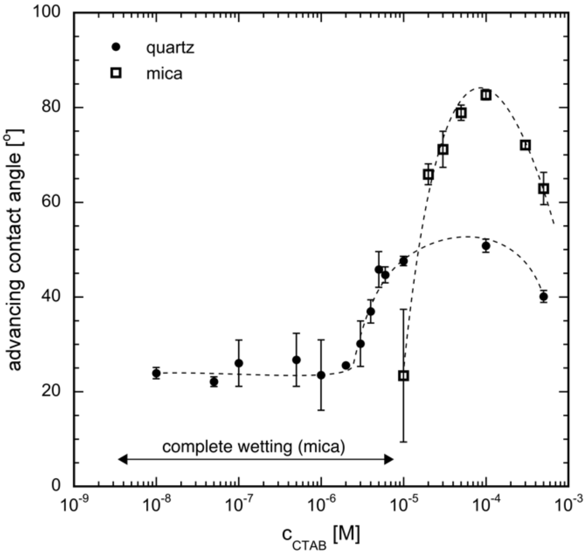

Fig. 2. Apparent advancing contact angles at quartz and mica surfaces as a function of CTAB concentration

Time of the three-phase contact formation by the colliding bubble at studied solid surfaces as a function of CTAB concentration is presented in Fig. 3. The data for t_{TPC} formed at L = "close" and "far" are presented there. For both mineral surfaces, two different trends of the t_{TPC} variations can be distinguished, depending on the CTAB concentration range. Initially, the t_{TPC} formed for L = "far" (t_{TPC}^{far}) is higher than that formed at L = "close" (t_{TPC}^{close}). After certain c_{CTAB} value (further called $c_{treshold}$), this trend is clearly inversed, i.e. $t_{TPC}^{far} < t_{TPC}^{close}$. This effect is more pronounced for quartz surface, because of smaller $c_{treshold}$ value, which is ca. 2×10^{-6} M. For mica surface $c_{treshold}$ is higher and equal to 3×10^{-5} M. This relation is visualized better in Fig. 4, where difference between TPC formed at location "close" and "far" (Δt) for studied surfaces are shown. It is worth mentioning that, for both quartz and mica, significant increase in the wetting film stability at $c_{CTAB} = 5\times10^{-4}$ M (i.e. for concertation where, most probably, CTAB bilayer formation process is initiated), was registered irrespective on the L value. For mica in $c_{CTAB} = 5\times10^{-4}$ M no TPC formation for location "close" was observed, while for location "far" the t_{TPC} was observed but was extremely prolonged ($t_{TPC} > 1$ s). For quartz surface t_{TPC} was noticed both for "far" and "close" locations with similar effect of severe prolongation ($t_{TPC} > 1$ - 2s). For clarity of Fig.s, this effect was not shown in Fig. 3 and 4. It is worth-mentioning that the TPC formation was observed starting from $c_{CTAB} = 1\times10^{-7}$ M for quartz and 5×10^{-7} M for mica, what stays is very good agreement with literature data on surface charge variations of liquid/gas and liquid/solid interfaces (see Introduction).

It has to be emphasized that, as already mentioned before, the t_{TPC} is composed of t_b and t_d. It was reported that t_b can be vital component of the whole time of the bubble attachment to the solid surface but its significance decreases with increasing of surface-active substance solution concentration (Kosior et al., 2014; Malysa et al., 2005). As was shown in (Zawala et al., 2017), the maximum differences in t_b for the bubble colliding with solid surface in solution of CTAB of concentration range 1×10^{-7} - 1×10^{-5} M was ca. 70 ms. Moreover, for $c_{CTAB} > 1\times10^{-5}$ M the t_b was as short as ca. 20 ms and depended no longer on CTAB concentration. Therefore, variations in the t_{TPC} presented in Fig. 3 and 4 cannot be explained by t_b decrease and have to be attributed mostly to modification of t_d values (Niecikowska et al., 2010;

Kosior et al., 2015). Explanation of the t_d variations in the studied system requires careful analysis of state of adsorption layer at both interfaces forming the wetting film, taking into account contact angle variations of the solid surfaces and formation of the DAL. This analysis is presented below.

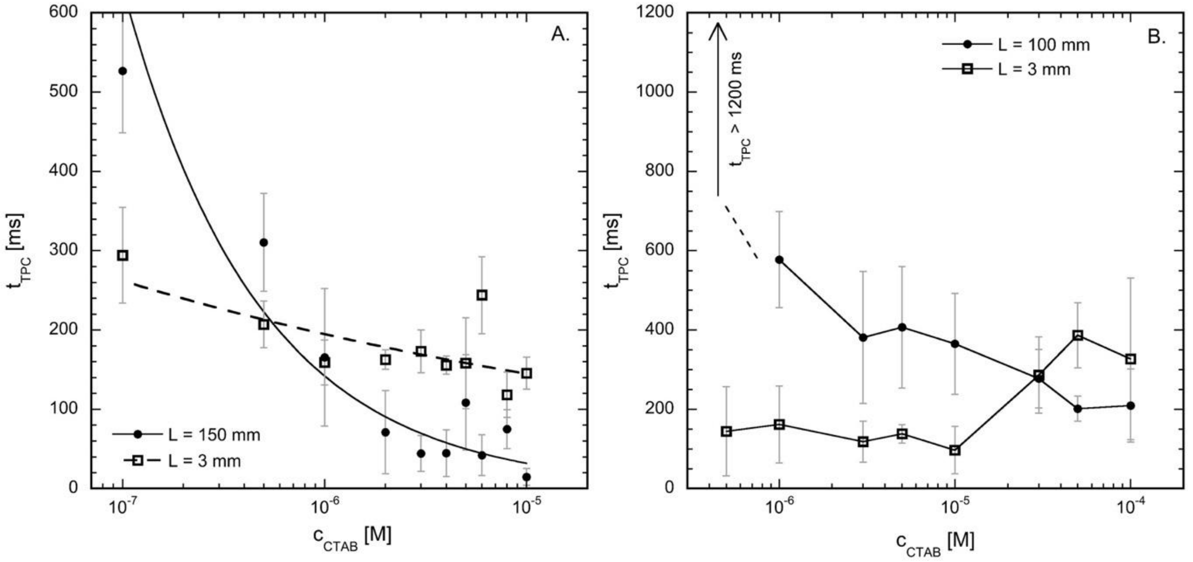

Fig. 3. Time of the TPC formation by the bubble colliding with (A) quartz surface and (B) mica surface in CTAB solutions of different concentrations. Both surfaces located "close" (L = 3 mm) and "far" (L = 100 - 150 mm) from the bubble formation point

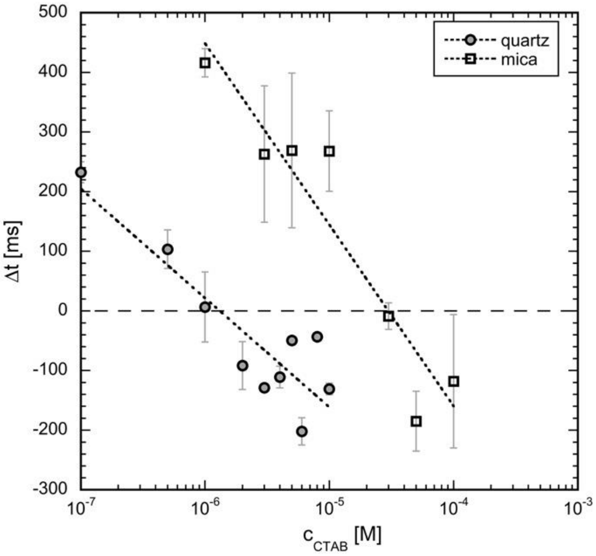

Fig. 4. Differences in the t_{TPC} formed at L = "far" (L = 100 - 150 mm) and "close" (L = 3 mm) in respect to the bubble formation point (Δt)

Fig. 5 presents schematic illustration of state of adsorption layer at both interfaces of the wetting film formed by the colliding bubble for L = "close" and "far" in two CTAB concentration regimes, causing different changes in the θ and the t_{TPC} values (see Figs. 3-4). Fig. 5A concerns low c_{CTAB} range ($c_{CTAB} < c_{threshold}$), where there was no θ changes and the $t_{TPC}^{far} > t_{TPC}^{close}$. This specific difference in the t_{TPC} was a consequence of different state of adsorption layer of CTAB molecules, preferentially adsorbed at the bubble surface in considered concentration range. For L = "close" the distance covered by the bubble after detachment from the orifice was too short for the DAL establishment, therefore adsorption coverage at liquid/gas interface was uniform. The bubble surface was positively charged from the very beginning of the wetting film formation (left picture in the Fig. 5A). In contrast, for L = "far" the DAL was formed at the distance covered by the bubble before collision with solid surface. Consequently, coverage at top liquid/gas interface forming the wetting film was depleted (right picture in the Fig. 5A). Thus, some additional time was needed to re-establish more uniform surface coverage suitable for liquid/gas interface charge reversal from negative to positive and liquid film destabilization by the electrostatic attraction forces. It was shown elsewhere (Niecikowska et al., 2010) that the calculated Δt values for considered concentration range ($c_{CTAB} < c_{threshold}$) is long enough for such uniform coverage re-establishment as a result of CTAB molecules adsorption from the bulk.

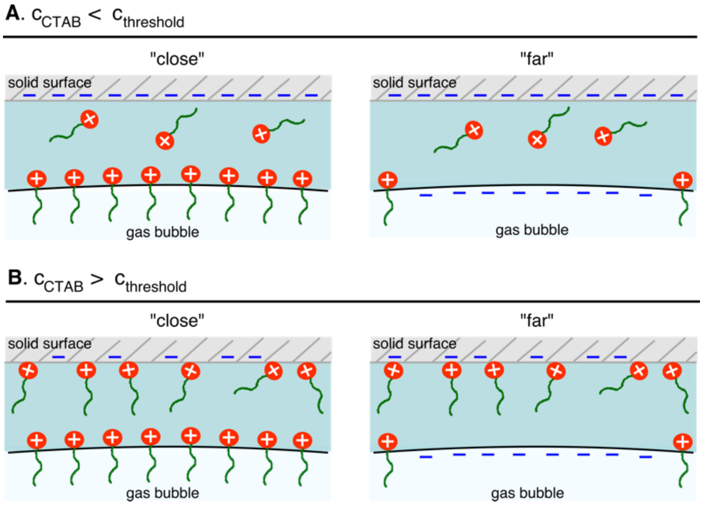

Fig. 5. Schematic illustration of state of adsorption layer at interfaces of wetting film formed by colliding bubble

Completely different situation can be observed for $c_{CTAB} > c_{threshold}$ regime (Fig. 5B), where increase in the θ start to be significant and inversion in the t_{TPC} values occurs, i.e. $t^{far}_{TPC} < t^{close}_{TPC}$. In this concentration range, CTAB molecules adsorb also at liquid/solid interface, causing (i) hydrophobization of the solid surface and (ii) screening out the negative solid surface charge. It is worth mentioning here that in considered system, solid surface hydrophobization could be caused by CTAB molecules adsorption from the bulk and by transfer of CTAB molecules from the bubble surface to solid surface during bubble attachment (Wang and Miller, 2018). Due to θ increase, the surface charge starts to be minor factor in liquid film stability (Stockelhuber 2003, Niecikowska et al. 2012, Zawala et al. 2017). Under such conditions it seems that hydrodynamic factor prevails over electrostatic and is responsible for inversion in the t_{TPC} values observed for $c_{CTAB} > c_{threshold}$ range. Due to higher adsorption coverage for L = "close", the drainage of the liquid film is slower comparing to L = "far", where liquid/gas interface can be fully or partially mobile (much smaller surface concentration). Certainly, similar situation is expected for $c_{CTAB} < c_{threshold}$ regime (Fig. 5A) but in this case faster liquid film drainage for L = "far" is compensated by necessity of re-establishment of adsorption coverage large enough for film destabilization by electrostatic interactions (bubble surface charge reversal). To check correctness of this hypothesis, we perform simple calculations based on Scheludko equation (Scheludko 1967), taking into account different mobility of the bubble surface.

Scheludko equation, describing drainage of wetting film, reads:

$$\frac{d(1/h^2)}{dt} = \frac{4}{3} n \frac{\Delta p}{\mu R_f^2} \tag{1}$$

where h is the film thickness, t is time, Δp is Laplace pressure, μ is liquid viscosity, R_f is radius of the liquid film and n is a parameter describing liquid/gas interface mobility, equal 1 for immobile (no-slip) and 4 for completely mobile (slip) surface. Basing of our hypothesis, for situation presented in Fig. 5B we can grant that n = 1 for L = "close" and n = 4 for L = "far". Assuming that for both L values the R_f and critical rupture thickness of wetting film is identical and that n is one and only parameter influencing film drainage kinetics we can rewrite the Eq. (1) in the form:

$$t_{close}/t_{far} = 4 \tag{2}$$

Now we can compare our experimental results with Eq. (2), assuming that drainage time is equal to t_{TPC} values for $c_{CTAB} > c_{threshold}$ regime (because bubble bouncing is practically completely damped). Average

t_{close}/t_{far} value calculated for quartz from 7 points presented in Fig. 4 (i.e. for $\Delta t < 0$) is equal to 4.1±3. For mica this value is smaller and equal 1.74±0.25, and was calculated from 2 points, only. Obtained t_{close}/t_{far} values indicate that postulated mechanism attributing hydrodynamics (mobility of the liquid/gas interface) as a factor responsible for different kinetics of the TPC formation at quartz and mica surface in the $c_{CTAB} > c_{threshold}$ regime is reasonable. The average t_{close}/t_{far} value for quartz was almost identical to that predicted by Eq. (2). For mica this value was significantly smaller, what is most probably caused by small number of data points taken for average calculations. It can be caused also by (i) only partial immobilization of the bubble surface at far position and/or (ii) small but still present contribution of solid surface charge, which could play some role in the considered phenomena.

3.2. Mixed n-octanol/CTAB system

Fig. 6 presents values of the t_{TPC} formed at quartz surface located at different L in mixed n-octanol/CTAB solutions of various composition, given in Table 1. Due to practical reasons explained in more details in the section 2.1, the experiments were conducted for "close" and "moderate" locations of the quartz/solution interface, i.e. 3 and 25 mm, respectively. It can be seen in Fig. 6 that the t_{TPC} values measured for L = 3 and 25 mm are practically identical. For the lowest n-octanol amount in the mixture, difference in the t_{TPC}^{close} and t_{TPC}^{far}values is quite small (ca. 20 ms). However, with increasing n-octanol amount, this difference significantly increases. Keeping in mind that the c_{CTAB} in all n-octanol/CTAB mixtures studied is smaller than 5×10^{-7} M (i.e. we are in the $c_{CTAB} < c_{threshold}$ regime – see. Figs. 2 - 3), we can conclude that this trend is opposite to that observed earlier in pure CTAB system (see Fig. 3).

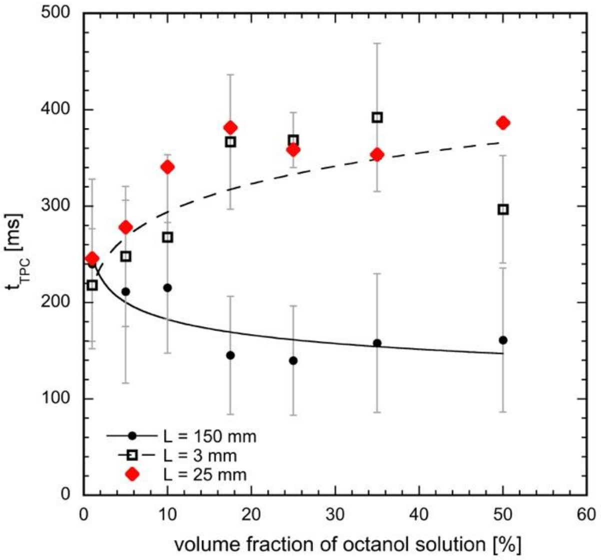

Fig. 6. Time of the TPC formation by the bubble colliding with quartz surface located at 3 mm ("close" distance), 25 mm ("moderate" distance) as well as 150 mm ("far" distance) from the capillary orifice (error bars for data determined at L = 25 mm not shown)

Small values of CTAB concentration in the studied mixtures (see Table 1) indicates that rupture of the liquid film is governed by electrostatic interactions, as shown and discussed above (section 3.1). It was confirmed that CTAB is essential component of the mixture, necessary for the wetting film destabilization and rupture – there was no TPC formation in water as well as pure n-octanol solution of concentration 1×10^{-3} M. Note, however, that the procedure of mixture preparation implied decrease in the CTAB concentration with increasing n-octanol amount. This is most probably the main reason of trend in the t_{TPC} variations observed in Fig. 6 for L = 3 and 25 mm. However, it cannot explain quite a big difference between "close/moderate" and "far" t_{TPC} values. Why does the t_{TPC}^{far} decreases with CTAB concentration decrease? Most probably, it is related to longer time available for CTAB molecules adsorption at the bubble surface. In the case of L = "far" this time is longer than for L = "close", because CTAB can be adsorb at the liquid/gas interface not only during bubble growing period (liquid/gas surface expansion at the capillary orifice) but also during its motion in the liquid. Longer distance covered by the bubble means longer adsorption time. As a result, for identical mixture composition, at location "far" the bubble collides with quartz surface with higher adsorption coverage comparing to the "close" position. It can be estimated from measured value of the bubble terminal velocity (15 cm/s) and distance *L* covered by the bubble before collision (150 mm) that the increase in adsorption time related to the bubble motion is equal to 1 s. This is rather small increase, however could be enough for faster induction of threshold concentration needed for the wetting film rupture (bubble surface charge reversal) and differences in the TPC formation kinetics. This situation seems more probable, when we take into account that increase of adsorption coverage related to the bubble motion can be also influenced by dynamic conditions, causing that adsorption is not only diffusion-controlled but resulted mainly from convection of the surfactant molecules to the rising bubble interface. At this point, we are not able to proof experimentally correctness of the above-mentioned hypothesis, explaining decrease in the t_{TPC}^{far} values with CTAB concentration decrease. We can, however, proof the hypothesis about t_{TPC} increase for "close" position, thanks to the adsorption time controlling device, developed in our laboratory.

To check correctness and reasonability of the hypothesis that increase in the t_{TPC}^{close} (Fig. 6) is related to decrease in c_{CTAB}, a following approach was applied. First, the time of the bubble growth at orifice was experimentally determined to be equal to $t_{growth} = 1.6$ s. Next, the adsorption coverage of the liquid/gas interface for adsorption time (t_{ads}) equal to t_{growth} was calculated for all values of c_{CTAB} in the mixture, on the basis of Ward-Tordai equation, using the software developed by Aksenenko (2001) and procedure described in (Kosior and Zawala, 2018). The results of calculations are presented in Fig. 7 (black dots). Then, the adsorption coverage for $c_{CTAB} = 4.95\times10^{-7}$ M established after $t_{ads} = t_{growth}$, equal to 0.17% was taken as a reference one (dashed line in Fig. 7). This reference coverage was used to calculate the time t^*, i.e. time necessary to establish adsorption coverage at the bubble surface equal to the reference one (i.e., equal to ca. 0.17%), for each CTAB concentration in the mixture. The values of t^* are presented in Table 2, while corresponding adsorption coverages are presented in Fig. 7 as hollow squares. It needs to be emphasized here that the calculations were made with assumption that n-octanol, present in the mixture, do not influence the CTAB adsorption kinetics. In reality, it could not be the case, therefore obtained results should be treated only as approximation.

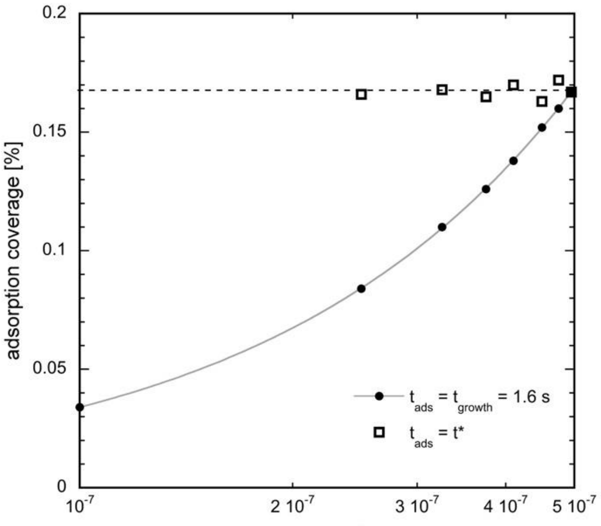

Fig. 7. Liquid/gas interface adsorption coverage for different adsorption times

Having the data presented in Table 2 we performed experiments, during which the device for adsorption time control was used to keep the initial adsorption coverage over the detaching bubble surface at the constant level. The bubble residue inside the "trap" was adjusted precisely, according to the t^* values determined. Due to practical reasons (bubble trap rotation delay), it was impossible to control the adsorption time smaller than 3 s, therefore the experiments were performed for $c_{CTAB} \leq$

4.1×10^{-7} M (see Table 2). The determined t_{TPC} values are presented in Fig. 8. As seen, all measured t_{TPC} are very close to each other and similar to that determined for c_{CTAB} = 4.95×10^{-7} M, i.e. our reference concentration in respect to the adjusted adsorption coverage. The trend observed in Fig. 6, where similar data without initial adsorption coverage controlling are presented, completely disappeared. It nicely confirmed that indeed, clearly noticeable increase in the t_{TPC} value for quartz surface for L = "close" is caused by decrease of concentration of CTAB in mixed solutions. These results show directly importance of surface charge in the wetting film stability and indicate that CTAB molecules are necessary for liquid film destabilization at negatively charged quartz surface. They also proof that n-octanol (non-ionic surface-active substance) alone cannot cause rupture of the wetting film in the considered system.

Table 2. Times needed to establish adsorption coverage of liquid/gas interface equal to 0.17% for different c_{CTAB} in the n-octanol/CTAB mixture

volume fraction of 1×10^{-3} M n-octanol solution [%]	c_{CTAB} [M]	t^* [s]
50	2.50×10^{-7}	39.8
35	3.25×10^{-7}	7.9
25	3.75×10^{-7}	4.0
17.5	4.10×10^{-7}	3.2
10	4.50×10^{-7}	2.0
5	4.75×10^{-7}	2.0
1	4.95×10^{-7}	1.6

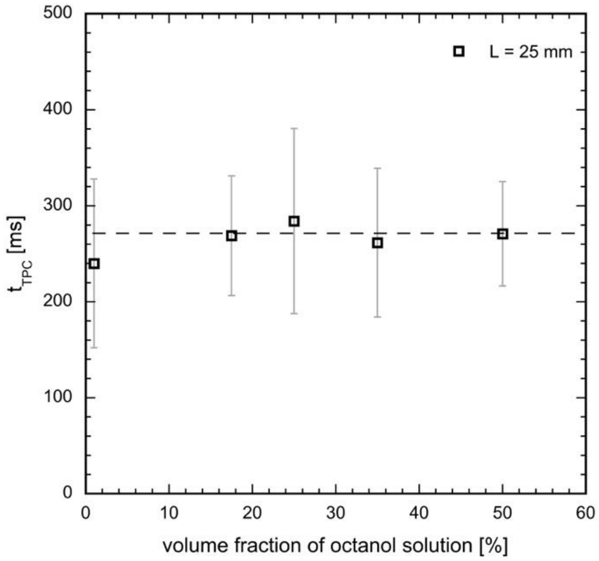

Fig. 8. Time of the TPC formation by the bubble colliding with quartz surface located at L = 25 mm from the bubble formation point – experiments with adsorption time control, leading to the equal (ca. 0.17%) initial adsorption coverage of CTAB molecules over the bubble surface (independently on CTAB concentration)

4. Conclusions

It was shown that dynamic adsorption layer formed at the bubble surface influences the kinetics of three-phase contact formation both at quartz and mica surfaces in pure and mixed solutions of surface-active substances. In pure CTAB solutions two regimes of concentration was distinguished, in which different mechanism of wetting film destabilization was observed. In low concentration regime (for quartz - c_{CTAB} < 2×10^{-6} M and for mica - c_{CTAB} < 5×10^{-5} M) the t_{TPC} was longer for distance L = "far" than

L = "close", because of different state of dynamic adsorption layer and the fact, that rupture of the wetting film was electrostatically driven. For distance L = "far", when the DAL was fully formed and top bubble adsorption coverage was depleted, additional time was needed for redistribution of CTAB molecules at the bubble surface and its charge reversal from negative to positive. However, in high concentration regime ($c_{CTAB} \geq 2\times10^{-6}$ M for quartz surface and $c_{CTAB} \geq 5\times10^{-5}$ M for mica surfaces), the relation between the t_{TPC} formed at various L was reversed due to increased hydrophobization of the solid surfaces. The wetting film rupture was governed by nucleation mechanism and the DAL presence changed hydrodynamics of the liquid film drainage. In studied n-octanol/CTAB mixtures quartz hydrophobicity was not affected, because n-octanol molecules adsorb only at gas/liquid interface, therefore wetting film rupture was governed by electrostatic interactions, similar to low concentration regime of pure CTAB solutions. Longer t_{TPC} for L = "close" resulted from lowering of the CTAB concentration in the mixture, what was proved by experiments with control initial bubble adsorption coverage. Shorter t_{TPC} for L = "far" was, most probably, a consequence of higher adsorption coverage of CTAB molecules at the bubble surface due to longer time available for adsorption, related to the bubble motion before the collision with solid surface interface immersed in mixtures of surface-active substances.

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