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BUBBLE COLLISIONS WITH HYDROPHOBIC AND HYDROPHILIC SURFACES IN α -TERPINEOL SOLUTIONS

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Influence of α -terpineol on phenomena occurring when a gas bubble approaches (collides with) hydrophilic (glass) and hydrophobic (Teflon) solid surfaces was revealed using high-speed camera (1182 frames/s). It was found that the bubble approaching the solid surface bounced backwards from the surface and its shape pulsed rapidly with frequency over 1000Hz. Number of the bouncing cycles and magnitude of the shape pulsations were decreasing with increasing α -terpineol concentrations. In distilled water the amplitude, frequency and number of the "approach-bouncing" cycles were identical at Teflon and glass interface. In of α -terpineol solutions a "necking" formation was recorded at Teflon surface, but not at the glass. The "necking" formation is a straightforward indication that the three-phase contact was formed. We found the most intriguing that a small amount of α -terpineol (adsorption coverage of 0.6%) sped-up and affected in such significant degree the bubble attachment to the hydrophobic surface. It was found that the induction time of the bubble attachment to Teflon was 5 milliseconds in α -terpineol presence. The average thickness of the thin liquid film separating the bubble and Teflon was estimated to be ca. 2,7 μm at the film rupture.

Key words: gas bubble, glas, Teflon, collision, α -terpineol

INTRODUCTION

Attachment of solid grains to air bubbles is a necessary condition of flotation, because the bubbles act as carriers transporting grains of useful ore component(s) to the froth layer. During flotation the bubbles and particles (independent of their nature, i.e. both hydrophobic and hydrophilic) are repeatedly brought together within the cell into positions of close encounters and/or collisions, necessary for formation of the

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bubble-grain aggregates. Collectors and frothers are two essential types of the reagents added into flotation system to modify properties of the solid/liquid and liquid/gas interfaces and enable separation of the useful grains of the ore from gangue minerals. Schulman and Leja (Schulman and Leja, 1954; Leja, 1956-57) pointed out the importance of the proper choice of the collector and frother because their molecules should interact to facilitate rupture of the liquid film and enable formation of the three-phase contact. Probability, P , of formation of a stable bubble-grain aggregate can be considered (Derjaguin and Dukhin, 1960; Schimmoler et. al., 1993; Ralston and Dukhin, 1999) as:

$$P = P_c P_a P_d \quad (1)$$

where P_c is the probability of collision, P_a is the probability of attachment (formation of the three phase contact) and P_d is the probability that detachment would not subsequently occur.

Probability of the collision is determined mainly by hydrodynamic conditions of the bubbles and particles motion. Surface properties of the solid/liquid and liquid/gas interfaces are decisive for attachment and detachment efficiencies. Thus, the differentiation between hydrophobic and hydrophilic particles occurs at these stages of the bubble-particle interactions (Leja, 1982). For formation of a stable bubble-particle aggregate the following processes have to take place (after particle and bubble collision): i) the syneresis and thinning of the liquid layer separating the bubble and particle to a critical rupture thickness, ii) the rupture of the liquid film and formation of a "hole" of the three phase contact, and iii) the expansion of the "hole" and formation of the perimeter of the three phase contact assuring stability of the bubble-particle aggregate. It is well-known that the hydrophobization of the surface of grains of useful component of the ore is a key factor for successful flotation separation. However, there is still a lot of unanswered questions and discussion related to the mechanism and time scale of the particle attachment to bubble, despite numerous studies addressing this problem (Nguyen et.al., 1997; Stechemesser and Nguyen, 1998; Schulze et.al., 2001; Yoon, 2000; Wang et.al., 2003; Gu et.al., 2003 - to mention only a few of the recent papers).

The paper presents results of studies of the influence of α -terpineol concentration on phenomena occurring when the bubble collides with solid hydrophilic and hydrophobic surfaces, and with free surface of the solution, as well. Rapid bubble pulsations ($f > 1000$ Hz) and bouncing from the solid surfaces and also the solution free surface were recorded and are described. Timescale of the bubble collisions, bouncing and attachment (when occurs) is presented for the interfaces studied.

EXPERIMENTAL

The experimental set-up is presented in Fig.1. It consists of the following main parts: i) a glass column with capillary and gas supply system, ii) recording camera, and iii) system of the movie transferring, splitting into single frames and image analysis.

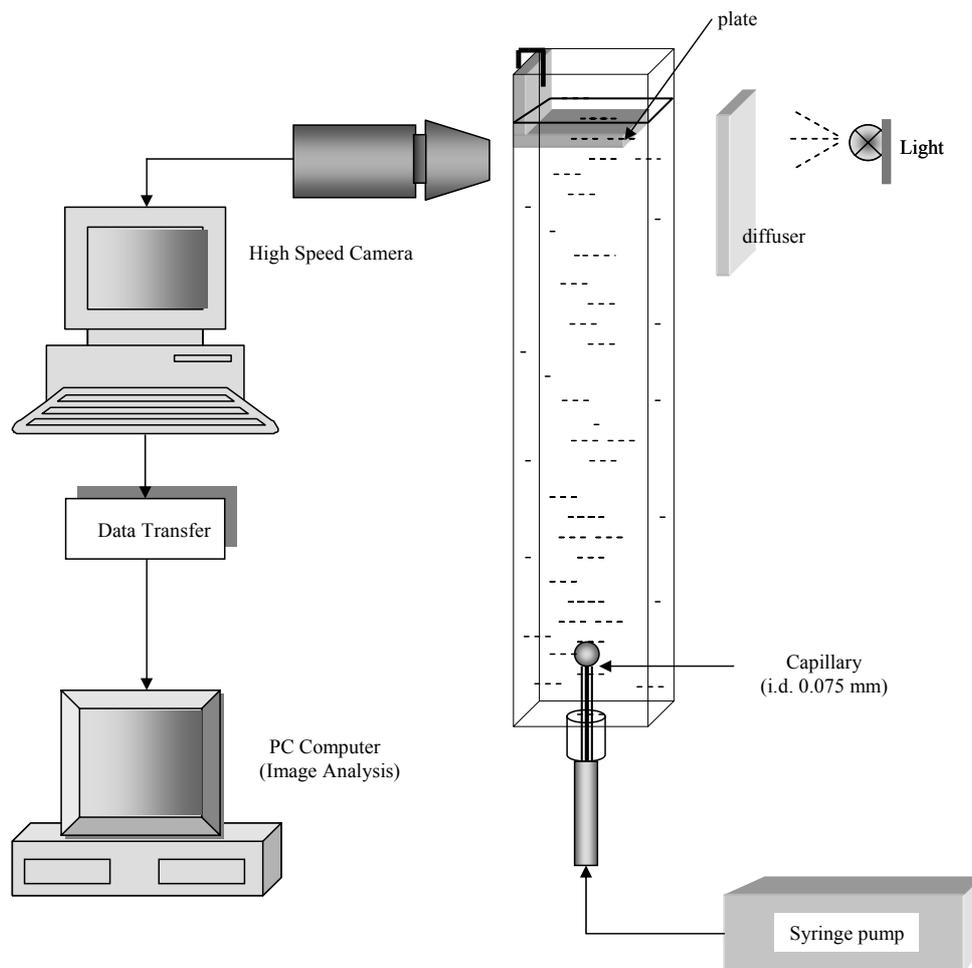


Fig. 1. Schematic of the experimental set-up

To avoid optical distortions the square glass column (50x50 mm) having at the bottom a capillary of inner diameter 0.075mm was used in the experiments. Bubbles were formed at the capillary orifice using the high precision (Cole-Parmer) syringe pump. At distance of ca. 30 cm from the capillary orifice (just beneath the solution surface) a glass (hydrophilic surface) or Teflon (hydrophobic surface) plate was mounted. Phenomena occurring when the bubble approached the solid surfaces and free surface of the solution were recorded. The movies were recorded using the high-speed (1182 frames per second) camera (with Cosmocar objective and rings for higher magnification). The movies obtained were transformed into BMP pictures and analyzed using a PC with SigmaScanPro Image Analysis Software. The distances between interface and bubble, subsequent positions of the bubble, and the bubble diameters were measured as a function of time. During collisions of the bubble with solid surface the bubble velocity variations were determined on the basis of measurements of the positions of the bottom pole of the bubble. To get absolute dimensions the image of nylon sphere of 3.89mm diameter was recorded after each experiment. The entire set-up was located on a vibration isolated laboratory table with an automatic levelling system.

Four-times distilled water and high purity α -terpineol were used for solution preparation. The glass and Teflon plates were cleaned with a chromic mixture and carefully washed-out with distilled water. The plates were immersed into solution studied for at least a few minutes (to have adsorption equilibrium) prior to the experiment. The experiments were carried out in room temperature.

RESULTS AND DISCUSSION

Figure 2 shows the sequences of frames illustrating the phenomena occurring when the rising bubble approaches Teflon (Fig. 2A) and glass (Fig. 2B) surface in α -terpineol solution of concentration $1 \cdot 10^{-5}$ M. Each subsequent picture shows the bubble position and its shape after time interval of 0.845 ms. Comparing both sets of the pictures one can immediately notice similarities and differences in the sequences of phenomena occurring during the bubble collision with Teflon and glass surfaces. In both cases: i) the bubble approaching the solids surfaces did not „stay“ immediately at the surface, but started to move backward, i.e. opposite to the direction of the buoyancy force, ii) the bubble shape pulsated rapidly, changing its shape during time intervals shorter than 0.845ms. The distinct difference in the collision course can clearly be noted on the frames showing the second approach of the bubble to these solid surfaces. In the case of glass (hydrophilic surface) the phenomena occurring during the bubble second approach are qualitatively similar as during the first one, i.e. the bubble bounced after collision and simultaneously its shape pulsated rapidly. However, in the case of Teflon (hydrophobic surface) a “necking” formation can be clearly seen after the bubble second approach. Such necking formation was described some time ago by Schulman and Leja (1958).

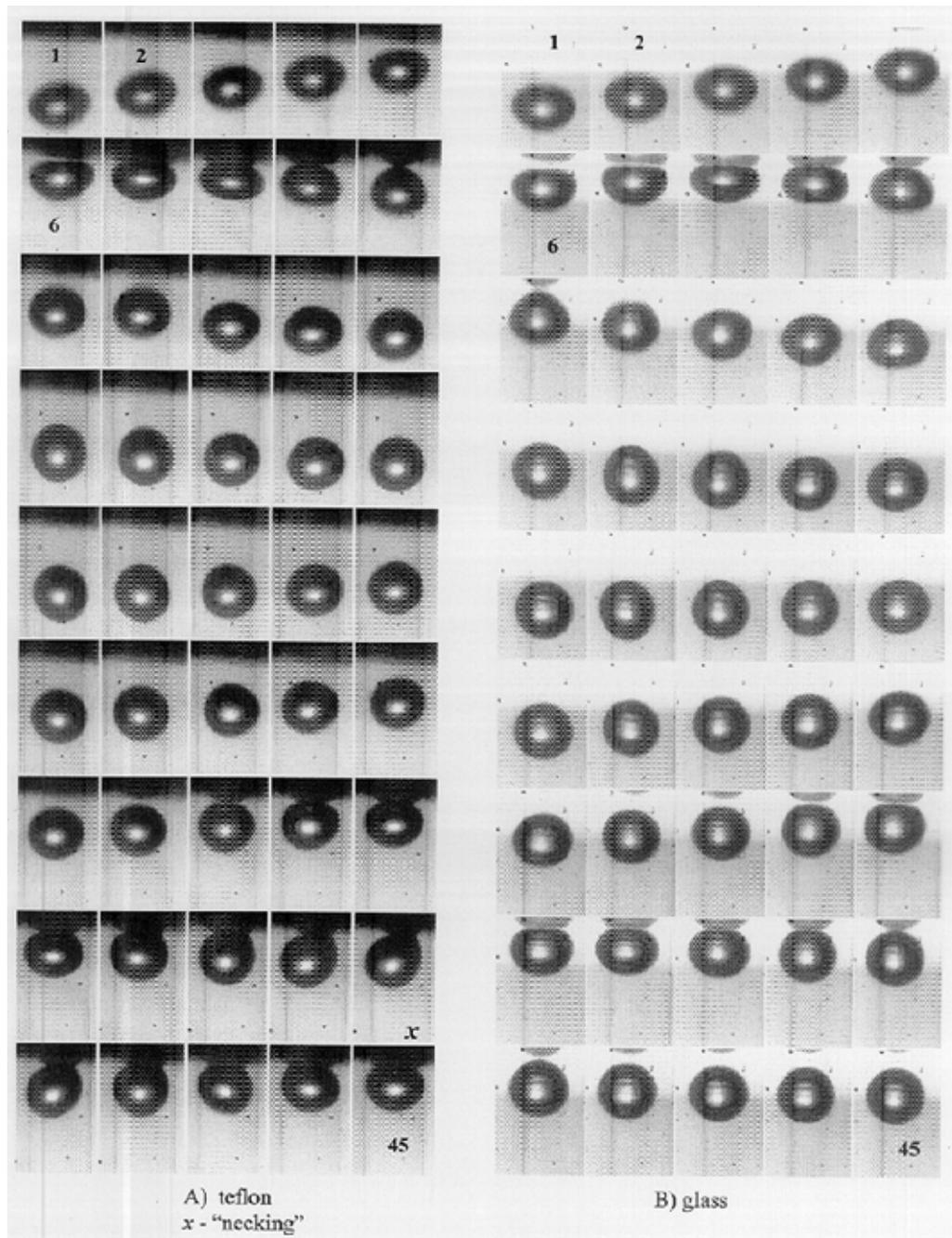


Fig. 2. Images of the bubble bouncing and pulsations in $1 \cdot 10^{-5}$ M α -terpineol solutions at the solid surfaces: A) Teflon, and B) glass. Time interval between every frame is 0.846 ms

Formation of this “necking” is a straightforward indication that the three phase contact solution-gas-Teflon was formed. As a result of the three phase contact formation the bubble was attached to Teflon surface and it’s bouncing was stopped.

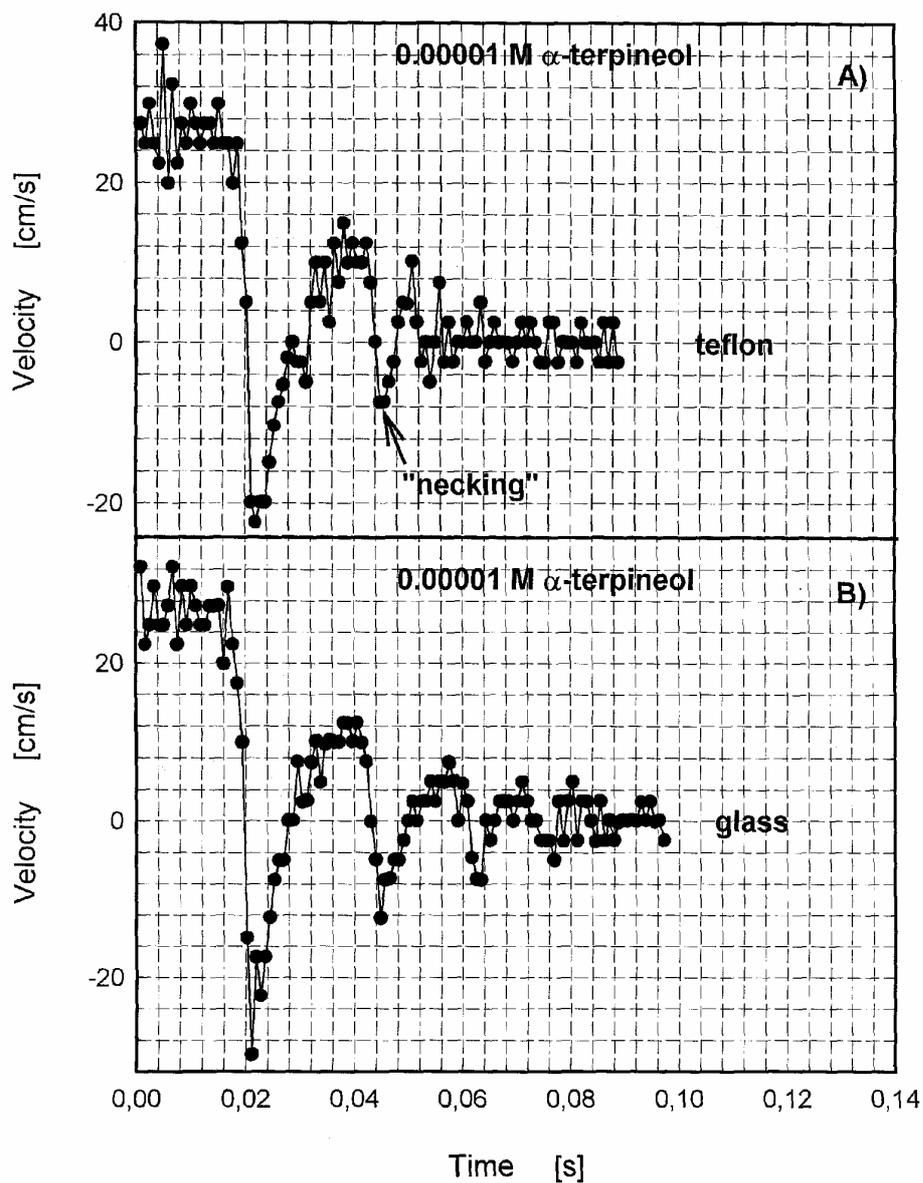


Fig. 3. Variations of the bubble velocity in $1 \cdot 10^{-5} \text{ M } \alpha\text{-terpineol}$ solution during the “approach-bouncing” cycles at: A) Teflon, and B) glass surface

The results of analysis of variations of the bubble velocity during collisions with solid hydrophobic (Teflon) and hydrophilic (glass) surfaces in $1 \cdot 10^{-5}$ M α -terpineol solution are presented in Fig. 3. As seen there the velocity of the bubble approach to the solid surfaces was constant (ca. 26.5 cm/s). On collision with Teflon (Fig. 3A) or glass (Fig. 3B) surface the bubble velocity was rapidly slowed down and then, the bubble moved backwards reaching the velocity up to 22-28 cm/s. Next, the bubble started second approach to the solid surface. It is worthy to underline how rapid this cycle was. As can be seen in Fig. 3 the timescale of the bubble velocity changing from +20 cm/s to -20 cm/s was 3-4 ms. Next, the bubble started its second approach to the surface, but the velocity of the second approach was lower (ca. 12 cm/s) as a result of the energy dissipation. During this second approach the bubble formed the three-phase contact with Teflon surface and, as a result of the bubble attachment to Teflon surface, the “necking” could be noticed (see Fig. 2A). In the case of glass, the three-phase contact was not formed and the bubble bounced again – there was no “necking” (see Fig. 2B). From the moment of the “necking” formation at Teflon surface there is clearly seen difference in the profiles of the bubble velocity variations at Teflon and glass surfaces (compare Fig. 3A and 3B). Attachment of the bubble to Teflon surface caused rapid damping of the bubble bouncing, while in the case of glass at least 2 additional cycles “approach-bouncing” were still detected (see Fig. 3B). As described above (Experimental) the instantaneous values of the bubble velocity were determined from measurement of the positions of the bottom pole of the bubble. Therefore, we believe that the velocity changes which can still be noted after the “necking formation” at Teflon surface (Fig. 3A) are in reality the bubble shape pulsations only. This is also confirmed by the fact that these velocity fluctuations are of significantly higher frequency than the real approach-bouncing cycles observed at the glass surface.

Data presented in Figs. 2 and 3 show straightforward that - as one could expect - the bubble attachment occurred at the hydrophobic surface, but not at the hydrophilic one. Moreover, they show that the timescale of the liquid film rupture and formation of the three-phase contact is of an order of a few milliseconds only. However, the importance of α -terpineol presence for the attachment to occur is rather unexpected and most intriguing. We have just found that without α -terpineol presence, i.e. in distilled water, the bubble attachment to Teflon surface was strongly hindered or at least slowed down.

Figure 4 presents the pictures of the bubble “approach-bouncing” cycles and its shape pulsations on collisions with Teflon (Fig. 4A) and glass (Fig. 4B) in distilled water. Variations of the bubble instantaneous velocities during the collisions are presented in Fig. 5 for Teflon (Fig. 5A) and glass (Fig. 5B). In distilled water the velocity variations of the “approach-bouncing” cycles are identical for Teflon and glass. Four distinct “approach-bouncing” cycles were detected both at Teflon and glass surfaces. Moreover, the amplitude and frequency of the velocity variations were identical on collisions with the hydrophobic and hydrophilic surfaces. There was no “necking” with the hydrophobic Teflon surface. Lack of the “necking” formation in

distilled water is also clearly seen on sequences of photos presented in Fig. 4. There are presented variations of the bubble shape and positions during 3 “approach-bouncing” cycles and no difference between collisions with Teflon and glass can be spotted.

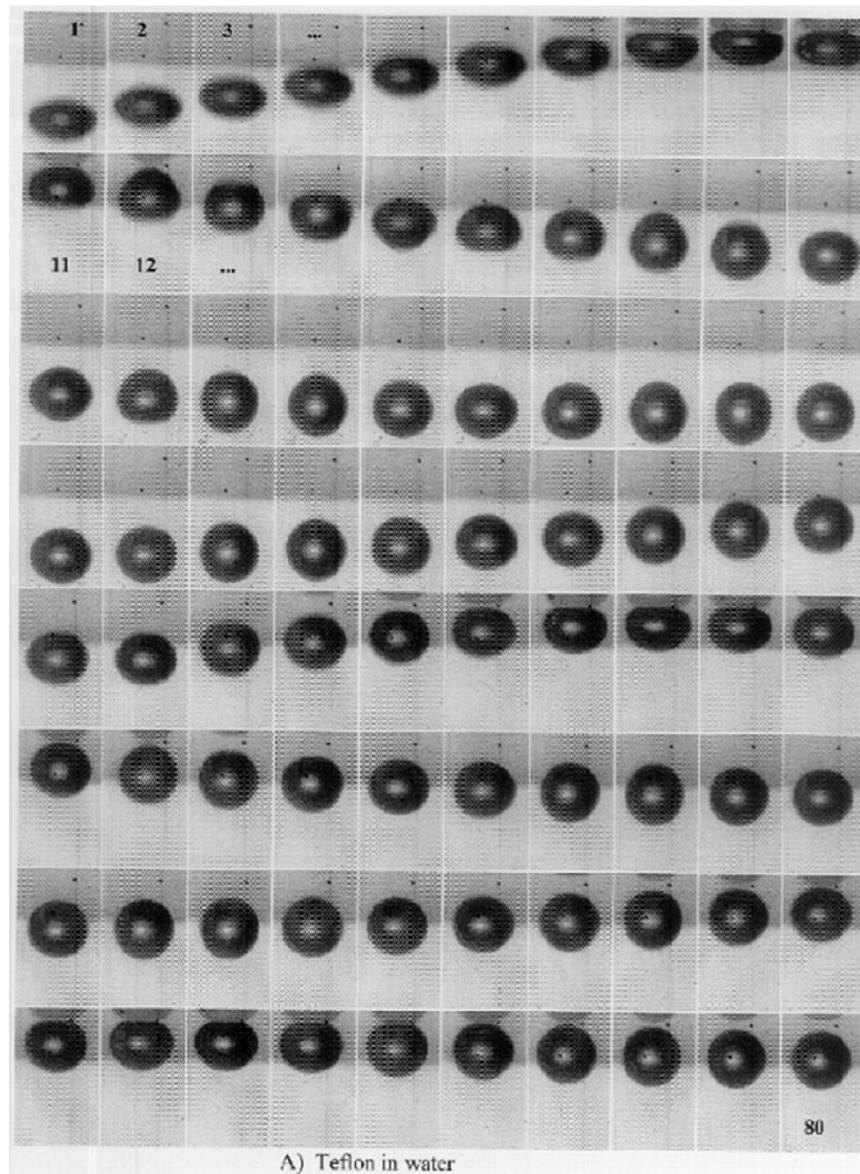


Fig. 4. Images of the bubble bouncing and pulsations in distilled water at: A) Teflon, and B) glass. Time interval between every frame is 0.846 ms

Certainly, we do not intend to claim that at longer time of contact the bubble will not be attached to the hydrophobic surface of Teflon. Surely, there will be formation of the three-phase contact and the bubble attachment to Teflon surface. However, we found it really fascinating how even this small amount of α -terpineol affected and sped-up the bubble attachment to the hydrophobic surface. At α -terpineol concentration of $1 \cdot 10^{-5}$ M the average adsorption coverage at bubble surface was 0.6% (Krzan and Malysa, 2002). Increasing α -terpineol concentration to $3 \cdot 10^{-5}$ M only (adsorption coverage - 1.8%) caused formation of the “necking” during the bubble first approach to Teflon surface, as showed in Fig. 6. There was no “necking” in the case of the glass surface (Fig.6B) and the bubble bounced backwards. This effect of α -terpineol presence on kinetics of the three phase contact formation with hydrophobic surface is really astonishing and confirms the Schulman-Leja theory (Schulman and Leja, 1954; Leja, 1956-57) about importance of frother in attachment of grains to bubble surface.

Data presented in Figs 2, 3 and 6 enable estimation of values of the induction time (Sven-Nilsson, 1934) for Teflon. The induction time is defined, generally speaking, as a minimum time of contact of the bubble and grain necessary to attach the grain to the bubble. Commonly, the induction time is measured by moving either a captive bubble in a solution toward and away of a bed of mineral grains or by moving the beds of grains toward and away from the bubble. In such measurements the induction time includes the times of: i) approach (collision), ii) film thinning, iii) film rupture, and iv) formation and spreading of the three phase contact. If we include all these stages into values of the induction time, which can be called $t_{ind.(max)}$, then we have the values of 26 and 5 ms for α -terpineol concentrations $1 \cdot 10^{-5}$ and $3 \cdot 10^{-5}$ M (see Figs. 3A and 6A), respectively. However, it seems more appropriate to consider, as was recently discussed by Gu et. al (2003) and Nguyen et. al. (1997), that the induction time consists only of the time required for film thinning, rupture and three phase contact expansion.

Bubble velocity profiles are an indication of the processes taking place during our experiments at solid surface. Far away from the interface the bubble moved with a constant terminal velocity in α -terpineol solutions (Krzan and Malysa, 2002). Decreasing and reversal of the bubble velocity means that the bubble was slowed down, stopped and bounced back as a result of the processes occurring in a thin liquid layer separating the bubble from solid surface. If the bubble did not bounce back but the “necking” formation was observed, then, during this time period the following processes occurred: i) drainage of the thin liquid film to a critical thickness of rupture, ii) rupture of the film and formation of the three phase contact, and iii) spreading of the tree phase contact spreading to a minimum radius required for a stable attachment. When the bubble bounces back without the “necking” formation it means that thin liquid film did not rupture and the three-phase contact was not formed. As seen from Figs. 2-6 only at the hydrophobic Teflon surface and in presence of α -terpineol the bubble attachment was observed. According to the discussion presented above the

time of the first approach-bouncing cycle in $1 \cdot 10^{-5}$ M α -terpineol solution should not be included in evaluation of the induction time values. Thus, as seen from Figs. 3 and 6 the real values of the induction time are 5 milliseconds, both for $1 \cdot 10^{-5}$ and $3 \cdot 10^{-5}$ M α -terpineol solutions.

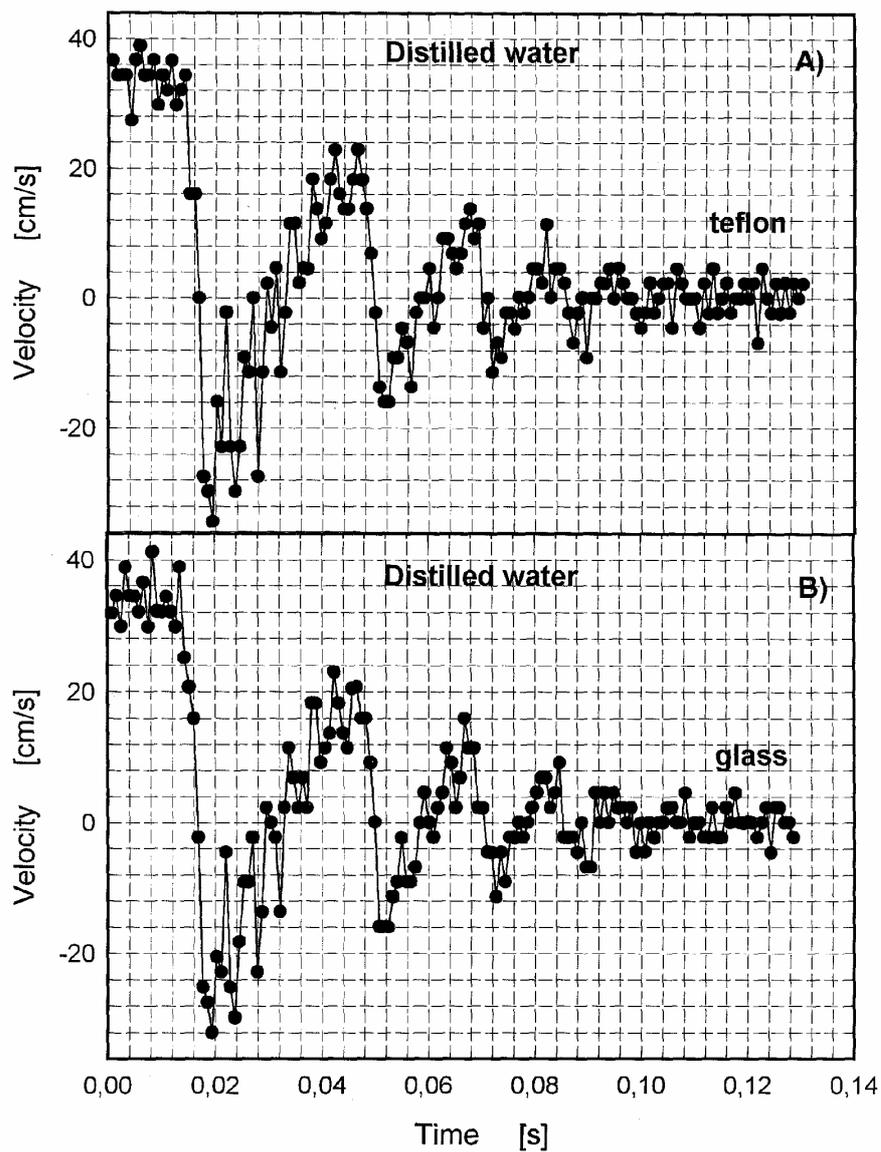


Fig. 5. Variations of the bubble velocity in distilled water during the “approach-bouncing” cycles at: A) Teflon, and B) glass surface

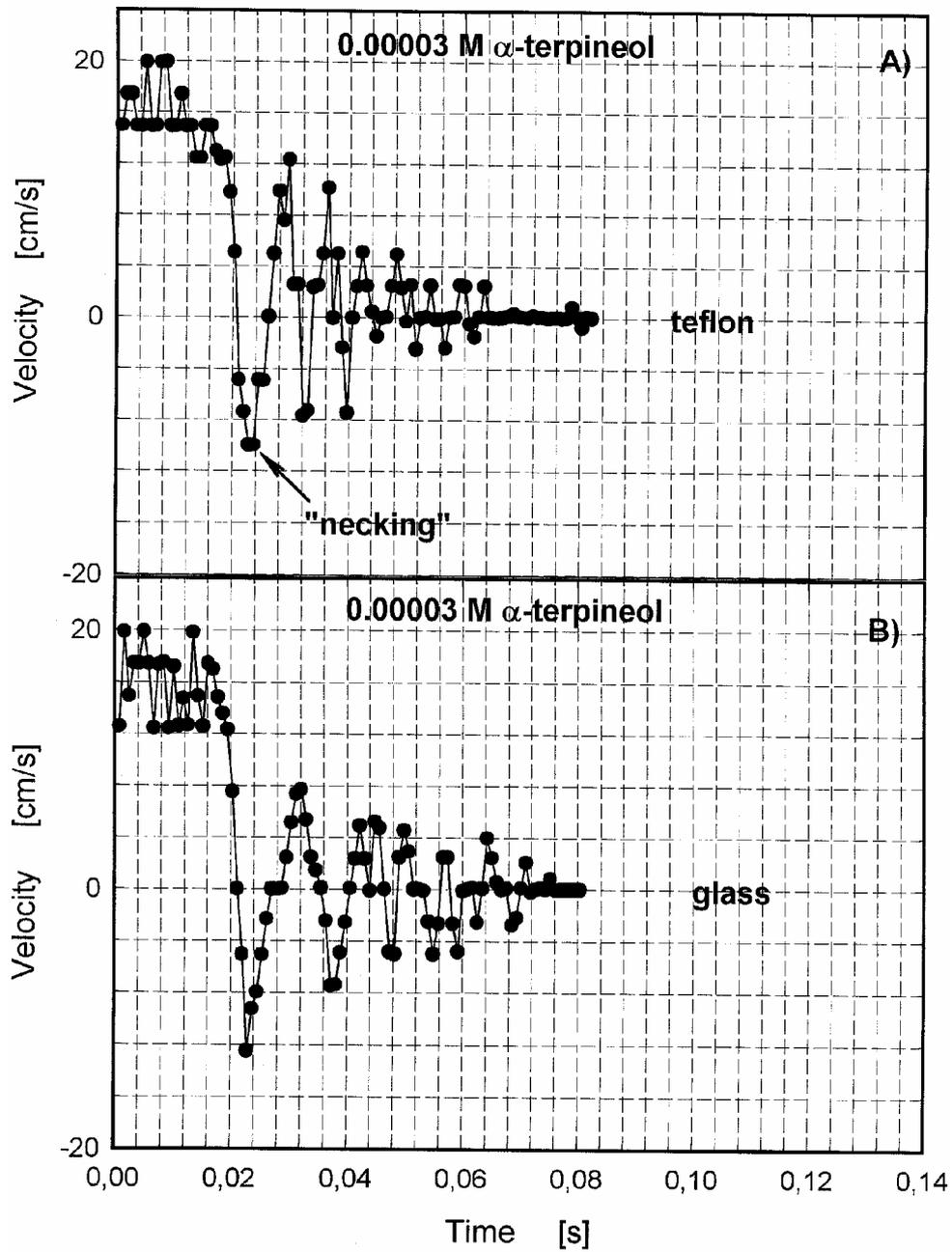


Fig. 6. Variations of the bubble velocity in $3 \cdot 10^{-5}$ M α -terpineol solution during the “approach-bouncing” cycles at: A) Teflon, and B) glass surface

We can also estimate an average thickness of the thin liquid film prior to its rupture at Teflon surface. According to Scheludko (1967) the thinning of the circular plane parallel film between a solid wall (non-slip conditions) and free surface (full mobility) can be described by the following relation:

$$\frac{d(1/h^2)}{dt} = \frac{16}{3\eta R_F^2} \Delta P \quad (2)$$

where h is the film thickness, t time, η viscosity, R_F radius of the film and ΔP difference between pressure in the thin film and pressure in bulk phase. After integration and assuming that at $t=0$, $h \Rightarrow \infty$ we obtain:

$$\frac{1}{h^2} = \frac{16}{3} \frac{\Delta P}{\eta R_F^2} t \quad (3)$$

From relation (4) the effective radius of the film formed by a bubble at interface can be found (Princen, 1969; Jachimska et al., 1998):

$$R_F^2 = \frac{FR_b}{\pi\sigma_{eq}} \quad (4)$$

where R_B is the bubble radius, σ_{eq} is the solution surface tension, and F is the total force causing the film thinning (buoyancy force, disjoining pressure, capillary force). Taking into account that:

$$\Delta P = \frac{2\sigma_{eq}}{R_b} \quad (5)$$

$$F = \frac{4}{3} \pi R_b^3 \rho g \quad (6)$$

we can obtain finally from Eqs. 3-6 that:

$$\frac{1}{h^2} = 8 \frac{\sigma_{eq}^2}{\eta \rho g R_b^5} t \quad (7)$$

where ρ is solution density and g gravity acceleration.

In the case of α -terpineol solution of concentration $1 \cdot 10^{-5}$ M the bubble radius $R_b = 0,07$ mm, $\sigma = 72.6$ mN/m, $g=9.81$ m/s, $\eta = 0.001$ Nsm⁻². Assuming, that the thinning time is equal to the induction time, i.e. $t = 5 \cdot 10^{-3}$ s we will obtain (Eq. 7) that the average thickness of the rupturing film was ca. 2.7 μ m. This value seems to be reasonable and of similar order as that one reported elsewhere (Malysa, 1998) for the rupture thickness of foam films in top layer of α -terpineol foams. Please, take into account that these values refer to the average thickness of the films. Certainly, in reality the thinning films are not plane parallel - there is a lot of thickness fluctuations and as a result locally, at the area of hole nuclei of the three phase contact formation, this rupture thickness can be smaller. Thus, the estimated average thickness should be treated as the highest limit of the thickness of the film rupture.

CONCLUSIONS

Bubble colliding with solid surface is not stopped immediately, but bounces backwards within timescale of a few milliseconds. Simultaneously, its shape pulsates rapidly with frequency over 1000Hz. Number of the bouncing cycles and magnitude of the shape pulsations was the highest in distilled water and was decreasing with increasing α -terpineol concentrations

In distilled water the amplitude, frequency and number of the “approach-bouncing” cycles were identical at hydrophobic (Teflon) and hydrophilic (glass) surfaces.

In α -terpineol a presence of “necking” formation was observed at the Teflon surface, but not at glass. The “necking” formation is a straightforward proof that the three-phase contact was formed. The induction time of the bubble attachment to Teflon was 5 milliseconds.

It was estimated, on the basis of the induction time determined, that the average thickness of the thin liquid film separating the bubble and Teflon was ca. 2.7 μ m prior to the film rupture.

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Wyznaczono wpływ α -terpineolu (spieniacz) na przebiegi procesów zachodzących w trakcie kolizji baniek powietrza z hydrofilową (szkło) oraz hydrofobową powierzchnia (teflon) ciała stałego. Uzyskano za pomocą szybkiej kamery (1182 klatki/s), zdjęcia procesów zachodzących podczas zderzenia bańki z powierzchnią ciała stałego o skrajnie różnych właściwościach hydrofobowo-hydrofilowych. Stwierdzono, że bańka dochodząca do powierzchni ciała stałego nie zostaje unieruchomiona, lecz może ulegać wielokrotnemu odbiciu i równocześnie jej kształt pulsuje z częstotliwością powyżej 1000 Hz. Pulsacje, liczba odbić i ich amplituda maleją wraz ze wzrostem stężenia α -terpineolu. W wodzie destylowanej liczba odbić i ich amplituda są identyczne zarówno przy powierzchni szkła jak i przy powierzchni teflonu. Natomiast w roztworach α -terpineolu zaobserwowano tzw. „necking” przy powierzchni teflonu, który dowodzi powstania trójfazowego kontaktu. Interesujący jest też fakt, że tak minimalne stężenie α -terpineolu (dające pokrycie adsorpcyjne 0.6%) umożliwiło i przyspieszyło utworzenie trójfazowego kontaktu z powierzchnia hydrofobową. Stwierdzono, że w badanych roztworach α -terpineolu czas indukcji w układzie bańka-teflon wynosił 5 ms. W oparciu o wyznaczony czas indukcji oszacowano, że średnia grubość filmu ciekłego rozdzielającego bańkę i teflon (w momencie jego przerwania) wynosiła ok. 2.7 μm .