| Physicochem. Probl. Miner. Process. 47(2011) 169-182 | Physicochemical Problems of Mineral Processing |
|------------------------------------------------------|---------------------------------------------------|
| www.minproc.pwr.wroc.pl/journal/ | ISSN 1643-1049 |

Received March 2, 2011; reviewed; accepted April 26, 2011

When and how α-terpineol and n-octanol can inhibit the bubble attachment to hydrophobic surfaces

Dominik KOSIOR, Jan ZAWALA, Kazimierz MALYSA

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Kraków, ncmalysa@cyf-kr.edu.pl

Abstract. Kinetics of the three phase contact (TPC) formation and phenomena occurring during collision of the rising bubble with Teflon plates of different surface roughness were studied in distilled water, α -terpineol and n-octanol solutions, using a high-speed camera of frequency 1040 Hz. Influence of solution concentration and surface roughness on time of the TPC formation and the time of drainage of the film formed between the colliding bubble and Teflon surface was determined. The surface roughness of the Teflon plates was varied within range 1-100 μ m. It was found that at small α -terpineol and n-octanol concentrations the time of the TPC formation was shortened in respect to distilled water. However, at their high concentrations the time of TPC formation was again longer and magnitude of this effect depended on the surface roughness. For example for Teflon surface of roughness 40-60 μ m the time of TPC formation was even 20-30 ms longer. The data obtained indicate that this effect is related to presence of air at the hydrophobic solid surfaces. The mechanism of this prolongation of the time of TPC formation due to the frother overdosage is proposed.

keywords: three phase contact, hydrophobic surface, frother, bubble collision, thin liquid film, surface roughness

1. Introduction

Frothers are reagents used in flotation mainly: i) for facilitation air dispersion into fine bubbles, ii) to prevent bubbles from coalescence (Cho and Laskowski, 2002a,b), iii) to assure formation of a froth layer of a suitable stability, and iv) to facilitate the three phase contact formation (Leja and Schulman, 1954). In flotation systems the three phase contact is formed in so-called elementary flotation act, that is, formation of stable bubble-grain aggregates as a result of the bubbles and grains collisions. For flotation separation the grains having hydrophobic surface need to form the three phase (TPC) contact and stay attached to the colliding bubble. Thus, kinetics of the TPC formation is of great importance for efficiency of the bubble attachment and flotation separation. For the TPC formation the liquid film separating the colliding bubble and grain surface needs to be ruptured during the collision time. Process of formation of the stable bubble-grain aggregate can be divided into three elementary steps: i) thinning of the liquid film formed by the colliding bubble to a critical thickness, ii) the film rupture and formation of a three-phase contact nucleus, and iii) expansion of three-phase contact line (Nguyen et al. 1997). As time of the film rupture and formation of a three-phase contact nucleus is significantly shorter than first sub-process so the process of film thinning is important to elucidate (Ralston et al., 2002) and seems to be the step determining kinetics of the three phase contact formation.

When the bubble collides with solid surface then a liquid layer (liquid film) separating the bubble and the solid surfaces starts to drain. For the TPC formation the draining film needs to reach its critical thickness of rupture. The kinetic of the liquid film drainage strongly depends on the film radius and properties of the film interfaces. Generally, the time needed to reach a definite thickness increases with the film size and depends on mobility of the film interfaces. When the mobility of the film interfaces is retarded, for example as a result of surfactant adsorption, then the time of the film thinning increases. In the case of wetting films the velocity of the thinning is. according to Scheludko equation (Scheludko, 1967), inversely proportional to the film radius and directly proportional to mobility of the film gas/solution interface, which is lowered in presence of an adsorption layer. Adsorption of surface active substances (frothers) can also significantly lower the bubble velocity (Krzan et al., 2004; Malysa et al. 2005, Kracht and Finch, 2010). Lower velocity of the rising bubble means a prolongation of the contact time during collision with particle and higher probability of the TPC formation. It is generally accepted that high hydrophobicity of solid surface is the factor ensuring the TPC formation and bubble attachment. However, it was showed recently (Malysa et al., 2005; Krasowska and Malysa, 2007) that even in the case of highly hydrophobic solid (Teflon of contact angle above 110°) the rising bubble was not attached during the first collision but could bounce a few times prior to the three phase contact (TPC) formation at the smooth solid surface (roughness below 1µm). The bubble bouncing is one of important factors leading to prolongation (up to over 80ms) the time of the TPC formation at Teflon surface.

This paper presents results of studies on influence of α -terpineol and n-octanol concentration on kinetics of the TPC formation and the bubble attachment to Teflon surfaces of different roughness. It was found that at high frother (α -terpineol and n-octanol) concentration the time of the TPC formation was prolonged. Mechanism of this important finding that a frother overdosage can inhibit the bubble attachment to hydrophobic surface is proposed.

2. Experimental

Phenomena occurring during the bubble collisions with and attachment to solid hydrophobic surfaces (Teflon plates) were monitored using the experimental set-up consisting of: (i) square glass column (50x50mm) with capillary of inner diameter 0.075mm at the bottom, (ii) high speed camera (SpeedCam MacroVis, 1040 frames per second), (iii) high precision pump with gas-tight syringe (Hamilton, 5ml), and (iv)

light source (optical fiber). The Teflon plate was positioned horizontally beneath the solution surface at the distance ca. L=250mm from the capillary orifice (bubble formation point). Single bubbles were formed at the capillary orifice and the time interval between each subsequent detaching bubble was 30s. The equivalent diameter of the bubble (d_{eo}) detaching from the capillary in distilled water was 1.48±0.03 mm. To record the bubble collisions and attachment the camera was positioned slightly below the solid/liquid interface with inclination of 3-4° in respect to the Teflon surface. The image of a nylon sphere of 3.89 mm diameter was recorded after each experiment for calculation of absolute dimensions of the bubble size. The movies recorded were analyzed either using the SigmaScan Pro Image Analyze Software and/or the WinAnalyze Motion Analyze Software. Variations of the bubble velocity during collisions with the Teflon plates were determined from measurements of subsequent positions of the bubble bottom pole. Further details of the experimental set-up and determination of the bubble velocity have been described elsewhere (Krasowska and Malysa, 2007; Malysa et al., 2005). All Teflon plates were prepared from the same piece of the commercial Teflon. Surface roughness of the Teflon plates was modified mechanically using an abrasive paper of grid numbers ranging from No. 2500 to No. 100. Figure 1 presents, as an example, the photos of the three Teflon surfaces (T2500, T1200 and T600) used in the experiments. Optical inverted microscope Nikon Epiphot 200 with magnification 20x was used to take the photos of the Teflon surfaces. Roughness of the Teflon plates was determined by measurements of the scratches sizes using SigmaScan Pro Image Analyze Software. Teflon 2500 was the solid with the smoothest surface (roughness $1-5\mu m$), while Teflon100 with the roughest one (roughness 80-100µm). The roughness of T1200 and T600 surfaces was 10-20 and 40-60 µm, respectively.



Fig.1 Photos of the Teflon surfaces of different roughness

The Teflon plates were carefully cleaned, using a chromic mixture. Next, they were washed-out with large quantity of 2-fold distilled water and then in the Milli-Q water. Next, the plates were boiled in the Milli-Q water for 1hour and stored in the Milli-Q water prior to the experiments. Measurements of the bubble collision and attachment to the Teflon surfaces of different roughness were performed in distilled water and in n-octanol (Fluka $\geq 99,5\%$) and α -terpineol (SAFC $\geq 96\%$) solutions of

various concentrations. The experiments were carried out at room temperature (20-22°C) and the distilled (Milli-Q) water used had the surface tension 72.4 mN/m and conductivity $0.05 \ \mu$ S/cm.

3. Results and discussion

The sequences of photos showing phenomena occurring during the bubble collisions in distilled water with Teflon surfaces of the roughness T600 and T2500 are presented in Fig. 2. As for a sake of comparisons the moment of the first collision was arbitrary denoted as the time t=0, so the negative time values refer to the bubble motion prior to the first collision. The photos of Fig. 2 clearly illustrate that, as reported earlier (Krasowska et al., 2007), the time of the bubble attachment to Teflon surface is strongly affected by the surface roughness. As seen there was no attachment to the Teflon2500 and Teflon600 surfaces during the first collision and the bubble bounced backward. However, the outcome of the second collision the situation was completely different. In the case of surface of higher roughness (Teflon600) the intervening liquid film was ruptured and the three phase contact (TPC) was formed, while the bubble bounced backwards from much smoother surface of Teflon2500. Moreover, there were up to five bouncing-approach cycles prior to the TPC formation and the amplitude of each subsequent bubble bounce was lowered as a consequence of dissipation of the kinetic energy associated with the bubble motion (E_k). The TPC was formed at Teflon2500 surface only after practically complete dissipation of the kinetic energy. The variations of the bubble velocity during collisions with the Telfon2500 and Teflon600 surface (see Fig. 2) are presented in Fig. 3. There are also defined two important parameters, the time of TPC formation (t_{TPC}) and the time of liquid film drainage (t_D) used for characterizing the kinetics of the three phase contact formation and the bubble attachment. As can be seen the t_{TPC} is the time interval from the moment of the bubble first collision till the moment of the TPC formation at the solid surface. It needs to be stressed here and remembered that as the t_{TPC} values cover also the bouncing periods of the colliding bubble so their magnitude can be affected by the bubble impact velocity - higher impact velocity leads to prolonged bouncing (Zawala and Malysa, 2011). The drainage time marked (t_D) is the time interval from the moment when the bubble stayed captured (practically "motionless") beneath the solid surface till the moment of the TPC formation. Thus, the t_D values depend only on stability of the thin liquid films formed by the colliding bubble. Determination of the starting point for the t_D measurements is a bit arbitrary because determination of the moment when the bubble stays "motionless" beneath the Teflon surface can be quite difficult. Therefore, the measurements were always repeated 20-40 times for each Teflon plate and the $t_{\rm D}$ values reported below are the mean values with different scatter - the scatter diminished with the surface roughness increase.

As described above and can be observed in Fig. 3 there was no attachment of the colliding bubble to either Teflon2500 or Teflon600 surface during the first collision. The bubble bounced backward (negative velocity values) and velocity of

each subsequent bubble approach to the plates was decreasing. In the case of Teflon2500, when the kinetic energy associated with the bubble motion was dissipated, the bubble stayed practically motionless till the moment of the TPC formation, which was easily detected due to rapid motion of the bubble bottom pole. In the case of the Teflon600 surface the TPC was formed during the second collision. Note please that the impact velocity of the bubble first collisions was the same in both cases. Despite this fact the significant difference in the t_{TPC} and t_D values for Teflon surfaces of different roughness are easily noticeable. In the case of Teflon2500 surface the t_{TPC} and t_D was 105±4 and 22±4ms, while for T600 the t_{TPC} and t_D was lowered to 37±2 ms and ca. 2ms, respectively.

Figure 4 presents the sequences of photos showing the bubble collisions with Teflon600 plate in $1 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ M α -terpineol solutions. It can be seen in Fig. 4 that α -terpineol presence, that is, the presence of a classical flotation frother (Gaudin, 1957; Leja, 1982; Laskowski, 1998), influenced the time of the bubble attachmet to the Teflon surface. At low α -terpineol concentration ($1 \cdot 10^{-5}$ M) the TPC was formed during the first collision and the t_{TPC} was ca. 2ms, i.e. was ca. 20 times shorter than in distilled water (see Figs 2 and 3).



Fig. 2. Sequences of photos of the bubble colliding in distilled water with Teflon2500 and Teflon600 surfaces. 0.96 ms is the time interval between subsequent photos of the sequence



Fig. 3. Variations of the bubble velocity during collisions with Teflon2500 (black circles) and Teflon600 (white triangles) surfaces in distilled water



Fig. 4. Sequences of photos of the bubble colliding with Teflon600 surface in of $1 \cdot 10^{-5}$ M and $1 \cdot 10^{-3}$ M α -terpineol solutions

Surprisingly however, the increased α -terpineol concentration $(1 \cdot 10^{-3} \text{ M})$ caused prolongation of the t_{TPC} from ca. 2 to 33±6 ms. Similar effect was observed also for high concentrations of n-octanol solutions. Figure 5 presents the comparisons of the velocity variations during collisions with Teflon600 surface in α -terpineol and noctanol solutions of low and high concentrations. The effect of the t_{TPC} prolongation at high concentrations of α -terpineol and n-octanol solutions is clearly seen in Fig. 5. At low concentration of these two frothers the TPC was formed during the first collision (t_{TPC} ca. 2ms) and the t_{TPC} were significantly longer (33 and 22 ms for α -terpineol and n-octanol, respectively) at their much higher (two orders of magnitude) concentrations. Note also please that at high α -terpineol and n-octanol concentrations the bubble impact velocity (velocity of the first collision) was smaller but still the t_{TPC} were longer despite diminished tendency for the bubble bouncing (Zawala et al., 2007).

Figures 6 and 7 present the dependences of the t_{TPC} and t_D values on concentrations a-terpineol (Fig. 6) and n-octanol (Fig. 7) for the Teflon surfaces of different roughness. Note please that only values of the time of liquid film drainage (t_D) (Figs 6A and 7A) are not affected by the bubble impact velocity and therefore they refer straightforward to stability of the liquid films formed by the colliding bubble. It is seen there that indeed, at high α -terpineol and n-octanol concentration the time of the liquid film drainage (Fig. 6B and 7B) were significantly prolonged and also values of the time of the TPC formation (Figs 6A nad7A) were higher, but not in every case. For the Teflon surface roughness within the range 1-60µm (Teflon2500 -Teflon600) the t_{TPC} values were significantly shorter in α -terpineol solutions of concentration 1.10⁻⁵ M and 6.10⁻⁵ M as well as n-octanol solutions of concentrations 6.10⁻⁶ and 3.10⁻⁵ M than those in distilled water. Further increase in concentration of both frothers, to $3 \cdot 10^{-4}$ M for α -terpineol and $6 \cdot 10^{-4}$ M for n-octanol, caused prolongation of the t_{TPC} , despite the fact that the bubble impact velocity was identical as in solutions of smaller (6.10⁻⁵ and 3.10⁻⁵ M for α -terpineol and n-octanol, respectively) concentrations. Thus, in these cases the t_{TPC} values were not affected by differences in the bubble impact velocity. In the case of the roughest surface (Teflon100) the t_{TPC} values were very short, ca. 1-3ms in distilled water, and practically did not change with a-terpineol and n-octanol concentration. Prolongation of the time of the film drainage, t_D, at high α -terpineol and n-octanol is clearly seen in Figs 6B and 7B. For the Teflon surface roughness within the range of 1-60µm (Teflon2500 – Teflon600) the t_D were the longest at $1 \cdot 10^{-3}$ M α -terpineol and $6 \cdot 10^{-4}$ M n-octanol concentration. There was practically no effect of α -terpineol and n-octanol concentration on the t_D values in the case of the roughest Teflon surface (Teflon100).



Fig. 5. Velocity variations during the bubble collision with Teflon600 surface in solutions of: (A) α -terpineol - concentration $1 \cdot 10^{-5}$ and $1 \cdot 10^{-3}$ M, and (B) n-octanol - concentration $6 \cdot 10^{-6}$ and $6 \cdot 10^{-4}$ M



Fig. 6. Values of (A) t_{TPC} and (B) t_D as a function of α-terpineol concentration for Teflon of different surface roughness



Fig. 7. Values of (A) t_{TPC} and (B) t_D as a function of n-octanol concentration for Teflon of different surface roughness

What is the mechanism responsible for prolongation of the time of the bubble attachment to hydrophobic surfaces at high α -terpineol and n-octanol concentrations? To explain it we need to consider in more details the phenomena occurring during the bubble collisions and immersion a hydrophobic surface into aqueous phase. Generally, the bubble colliding with any interface can either bounce or rupture (free surface) or form the three phase contact (hydrophobic surface) or stay captured (hydrophilic solid surface). The bubble bouncing is a consequence of competition between two simultaneous processes (Chester and Hofman 1982, Zawala et al. 2007): (1) thinning of the intervening liquid film; and (2) the increase of the free energy of the system resulting from the surface area increase due to the deformation of liquid/gas interface. During the collision of the rising bubble a dissipation of energy associated with the bubble motion takes place what causes decrease in the bubble shape pulsations and the

amplitude of each subsequent approach-bounce cycle. This effect is more pronounced in distilled water (see Fig. 2) due to highest impact velocity of the colliding bubble. The bubble bouncing is the reason that for the Teflon plates of the smallest roughness the time of the TPC formation (t_{TPC}) was significantly longer than the time of the liquid film drainage (t_D). For the roughest Teflon surfaces the t_{TPC} and t_D values were practically identical because the drainage and rupture of the intervening liquid film occurred during the first collision - there was no bouncing of the bubble.

In our previous papers (Malysa et al. 2005, Krasowska and Malysa 2007, Krasowska et al. 2007) two possible mechanisms, explaining the influence of roughness on kinetics of the TPC formation and the bubble attachment to hydrophobic solid surface in distilled water, were proposed. The crucial role of roughness of the hydrophobic solid surface, affecting time scale of TPC formation and bubble attachment, was attributed to: (i) local differences in radius of the liquid film formed at irregularities and pillars of rough solid surface, and (ii) presence of air entrapped in surface scratches and irregularities of the hydrophobic surface. The first mechanism takes into account fact that kinetics of the liquid film drainage is strongly affected by the film lateral dimensions – smaller film radius means that time needed for the film to reach a definite thickness is shorter. At rough hydrophobic surface the TPC can be formed due to rupture of various local wetting films formed at pillars of the rough surface. As lateral dimensions of such local wetting films are much smaller than radius of the entire liquid film formed by the colliding bubble so these films need shorter time to drain to a critical thickness of their rupture. This mechanism seems to be most probable for surfaces of highest roughness, i.e. in the case of Teflon100 plates. The second mechanism postulated takes into account influence of air presence at hydrophobic surface on kinetics of the TPC formation by the colliding bubble. It is worthy to add here that in studies on long range attractive interactions between hydrophobic bodies immersed into solution it was showed in 2000 (Ishida et al. 2000), using the TM AFM, that nanobubbles were attached to the hydrophobic surfaces immersed into aqueous solution. A number of papers documenting existence of nanobubbles at hydrophobic surfaces is increasing rapidly (Ishida et al., 2000; Tyrrel and Attard, 2002; Attard, 2003; Steitz et al., 2003; Nguyen et al., 2003; Yang et al., 2003; Zhang et al., 2006,). As high affinity to air is a typical feature of hydrophobic surfaces so air can be entrapped in scratches of hydrophobic surface during its immersion into aqueous phase. The mechanism of air entrapment during immersion of the Teflon plate into water (see Fig. 8) was described in details elsewhere (Krasowska et al., 2007; Krasowska et al., 2009) and it was showed that the amount of air entrapped was increasing with roughness of the hydrophobic surface. Thus, diminishing the t_{TPC} values with surface roughness can be a consequence of coalescence of the colliding bubble with nano and/or microbubbles present at larger amounts at rougher hydrophobic surface. In the case of smooth hydrophobic surface the amounts of entrapped air is lower and therefore the t_{TPC} values are higher. The results presented above strongly support the hypothesis put forward in our previous

papers (Krasowska and Malysa, 2007; Krasowska et al., 2007; Krasowska et al., 2009) that air is entrapped at hydrophobic surfaces and its presence can significantly affect kinetics of the TPC formation. As can be observed in Figs 6 and 7 in distilled water, devoid of any surface active substances, the t_{TPC} values were monotonically decreasing with increasing roughness of the Teflon plates. This effect can be attributed to increase in amount of air entrapped into the solid surface irregularities. As more air can be captured at rougher surface so the probability is higher that the bubble hit the area where air (in form of nano- and miro-bubbles) is present.



Fig.8. Schematic illustration of the liquid (foam) film formed in a frother solution between the colliding bubble and air micro- and/or nano-bubbles present at Teflon surface

The mechanism of inhibition of the bubble attachment at high α -terpineol and n-octanol concentrations, due to air presence at hydrophobic surface, is depicted schematically in Fig. 8. When air is present at hydrophobic surface then the colliding bubble hits micro- and/or nano-bubbles present and already having locally formed three phase contact of very small perimeter. In solutions of any surface active substance (each flotation frother) an adsorption layer is formed at solution/gas interface, that is, at the colliding bubble surface and at surfaces of the micro- and/or nano-bubbles attached to Teflon surface. Thus, instead of a wetting film formed between solid surface and the colliding bubble surface there are formed locally the symmetric (foam) films between the colliding macro-bubble and the micro- and/or nano-bubbles attached to the Teflon surface. It also means that rupture of the film and the TPC formation is occurring as a result of bridging (coalescence) of the colliding bubble and nano- or sub-microscopic bubbles already attached to the Teflon surface. As it is well known that stability of symmetric foam films increases with surfactant concentration (Exerowa and Kruglyakow, 1998) so the prolongation of the time of the TPC formation and the time of the film drainage in α-terpineol and n-octanol of high concentration is a strong evidence that there were locally the foam films formed, that is, there were air micro-bubbles attached to the Teflon surfaces. In distilled water and low concentrations of α -terpineol and n-octanol solutions the stability of those foam films formed locally was low because either there was no adsorption layer (distilled water) or the adsorption coverage's were too low to assure a sufficient stability of these local foam films. Moreover, velocity of the film drainage decreases with surfactant concentrations (adsorption coverage) due to immobilization of the solution/air interfaces (Exerowa et al., 2003). Results of studies on critical coalescence concentration (CCC) (Cho and Laskowski, 2002a,b), which show that the bubble coalescence is stopped above the CCC value (Cho and Laskowski, 2002a,b; Grau et al, 2005; Szyszka et al, 2006; Grau and Laskowski, 2006), indicate also that increased frother concentration leads to increased stability of the thin liquid films. Lack of the bubble coalescence means that stability of the liquid film formed between colliding bubbles is increased and therefore there is no bubble coalescence.

4. Concluding remarks

It was found that the time of the three phase contact formation at hydrophobic surface (Teflon) by colliding bubble is strongly affected by frother (α -terpineol, noctanol) presence in the system. Low concentrations of α -terpineol and n-octanol caused that the time of the TPC formation and the time of drainage of the liquid film separating the colliding bubble from Teflon surface were shortened. This effect was also dependent on the solid surface roughness. At high solutions concentration the opposite effect was observed, that is the t_{TPC} and t_D values were higher. This is rather surprising but important finding because it straightforwardly shows that overdosage of a frother can be disadvantageous for flotation efficiency. The mechanism of prolongation of the time of the bubble attachment to hydrophobic surfaces at high frother concentrations is described in details. This effect is attributed to a presence of air at the hydrophobic surfaces in a form of micro- and/or nano-bubbles. When air is entrapped in cavities of hydrophobic surface then foam films are formed locally between the micro- and/or nano-bubbles and the colliding bubble. Stability of these foam films is increased at high α -terpineol, n-octanol concentrations and therefore the time of the bubble attachment was prolonged.

Acknowledgements

This work was supported by the "Krakow Interdisciplinary Ph.D. Project in Nanoscience and Advanced Nanostructures" operated within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund and MNiSW grant No. NN204 133640.

References

- ATTARD P., 2003. Nanobubbles and the hydrophobic attraction, Adv. Colloid Interface Sci., 104, 75-91.
- CHESTER A. K., HOFMAN G., 1982. Bubble Coalescence in Pure Liquids, Appl. Sci. Research, 38, 353-361.
- CHO Y.S., LASKOWSKI J.S., 2002a. *Effect of flotation frothers on bubble size and foam stability*, Int. J. Miner. Process., 64, 69–80.
- CHO, Y.S., LASKOWSKI, J. S., 2002b, *Bubble Coalescence and Its Effect on Bubble Size and Foam Stability*, Canadian J. Chem. Eng. 80, 299-305.
- EXEROWA D., KRUGLYAKOV P.M., 1998. Foam and Foam Films Theory, Experiments, Application, Elsevier, Amsterdam.
- EXEROWA D., CHURAEV N.V., KOLAROVA T., ESIPOVA N.E., PANCHEV N., ZORIN Z.M., 2003. Foam and wetting films: electrostatic and steric stabilization, Adv. Colloid Interface Sci., 104, 1–24.
- GAUDIN A.M., 1957. Flotation, McGraw-Hill, New-York.
- GRAU R.A., LASKOWSKI J.S., HEISKANEN K., 2005. *Effect of frothers on bubble size*, Int. J. Miner. Process., 76 (4), 225-233.
- GRAU R.A., LASKOWSKI J.S., 2006. Role of frothers in bubble generation and coalescence in a mechanical flotation cell, Canadian J. Chem. Eng. 84 (2), 170-182.
- KRASOWSKA M., MALYSA K., 2007. Wetting films in attachment of the colliding bubble, Adv. Colloid Interface Sci., 134–135, 138–150.
- ISHIDA N., INOUE T., MIYAHARA M., HIGASHITANI K., 2000. Nano Bubbles on a Hydrophobic Surface in Water Observed by Tapping-Mode Atomic Force Microscopy, Langmuir, 16, 6377-6380
- KRASOWSKA M., KRASTEV R., ROGALSKI M., MALYSA K., 2007. Air-Facilitated Three-Phase Contact Formation at Hydrophobic Solid Surfaces under Dynamic Conditions, Langumir, 23, 549-557.
- KRASOWSKA M., ZAWALA J., MALYSA K., 2009. Air at hydrophobic surfaces and kinetics of three phase contact formation, Adv. Colloid Interface Sci., 147–148, 155–169.
- KRZAN M., LUNKENHEIMER K., MALYSA K., 2004. On the influence of the surfactant's polar group on the local and terminal velocities of bubbles, Colloids Surfaces A, 250, 431-441.
- KRACHT W., FINCH J.A., 2010. *Effect of frother on initial bubble shape and velocity*, J. Miner. Process., 94, 115–120.
- LEJA J., SCHULMAN J.H., 1954. Flotation Theory: Molecular Interactions between Frothers and Collectors at Solid-Liquid-Air Interfaces, Trans. AIME, 199, 221-228.
- MALYSA K., KRASOWSKA M., KRZAN M., 2005. Influence of surface active substances on bubble motion and collision with various interfaces, Adv. Colloid Interface Sci., 114-115, 205-225

- NGUYEN A.V., SCHULZE H.J., RALSTON J., 1997. *Elementary steps in particle-bubble attachment*, Int. J. Miner. Process., 51, 183-195.
- NGUYEN A.V., NALASKOWSKI J., MILLER J. D., BUTT H-J., 2003. Attraction between hydrophobic surfaces by atomic force microscopy, Int. J. Miner. Process., 72, 215–225.
- RALSTON J., DUKHIN S.S., MISHCHUK N.A., 2002. Wetting film stability and flotation kinetics, Adv. Colloid Interface Sci., 95, 145-236.
- SCHELUDKO A., 1967. Wetting film stability and flotation kinetics, Adv. Colloid Interface Sci., 1, 391-464.
- STEITZ R., GUTBERLET T., HAUSS T., KLÖSGEN B., KRASTEV R., SCHEMMEL S., SIMONSEN A.C., FINDENEGG G. H., 2003. Nanobubbles and their precursor layer at the interface of water against a hydrophobic substrate, Langmuir, 19, 2409– 2418.
- SZYSZKA D., DRZYMAŁA J., ŁUCZYŃSKI J., WILK K.A., PATKOWSKI J., 2006. Concentration of α-terpineol and (2-dodecanoyloxyethyl)trimethyl ammonium bromide required for prevention of air bubble coalescence in aqueous solutions, Physicochemical Problems of Mineral Process., 40, 53-59
- TYRREL J.W.G., ATTARD P., 2002. Atomic Force Microscope Images of Nanobubbles on a Hydrophobic Surface and Corresponding Force-Separation Data, Langmuir, 18, 160-167.
- YANG J., DUAN J., FORNASIERO D., RALSTON J., 2003. Very small bubble formation at the solid–water interface, J. Phys. Chem. B, 107, 6139–6147.
- ZAWALA J., KRASOWSKA M., DABROS T., MALYSA K., 2007. Influence of Bubble Kinetic Energy on its Bouncing During Collisions with Various Interfaces, Can. J. Chem. Eng., 85, 669–678.
- ZAWALA J., MALYSA K., 2011. Influence of the Impact Velocity and Size of the Film Formed on Bubble Coalescence Time at Water Surface, Langmuir, 27 (6), 2250-2257.
- ZHANG H. X., MAEDA N., CRAIG V. S. J., 2006. Physical Properties of Nanobubbles on Hydrophobic Surfaces in Water and Aqueous Solutions, Langmuir, 22, 5025-5035.

Kosior, D., Zawala, J., Malysa, K., Kiedy i w jaki sposób α -terpineol and n-octanol mogą opóźniać (hamować) przyczepienie pęcherzyka do hydrofobowych powierzchni, Physicochem. Probl. Miner. Process., 47 (2011) 169-182, (w jęz. ang.)

Badano kinetykę powstawania kontaktu trójfazowego podczas kolizji pęcherzyka w wodzie i w roztworach α-terpineolu i n-oktanolu z płytkami Teflonowymi o różnej szorstkości powierzchniowej, przy użyciu szybkiej kamery o częstotliwości 1040Hz. Określono wpływ stężenia substancji powierzchniowo aktywnych i szorstkości powierzchniowej na czas powstawania kontaktu trójfazowego i czas wyciekania cienkiego filmu ciekłego powstającego pomiędzy pęcherzykiem i powierzchnią Teflonu. Szorstkość powierzchniowa Teflonu była modyfikowana w zakresie 1-100 μm. Wykazano, że w roztworach o małych stężeniach α-terpineolu i n-oktanolu czas powstawania kontaktu trójfazowego uległ

D. Kosior, J. Zawala, K. Malysa

skróceniu w porównaniu do wartości zmierzonych w czystej wodzie. Jednakże, przy wysokich stężeniach badanych spieniaczy następowało znowu wydłużenie czasu powstawania kontaktu trójfazowego, a wielkość tego efektu była uzależniona od szorstkości powierzchni płytki teflonowej. Przykładowo dla płytki teflonowej o szorstkości powierzchniowej 40-60 µm czas powstawania kontaktu trójfazowego uległ wydłużeniu nawet o 20-30 ms. Wyniki uzyskane wskazują, że efekt ten jest związany z obecnością powietrza na hydrofobowej powierzchni ciała stałego. W pracy przedstawiono mechanizm wydłużenia czasu powstawania kontaktu trójfazowego przy nadmiernej dawce spieniacza.