

Received June 23, 2017; reviewed; accepted July 24, 2017

Influence of bubble approach velocity on coalescence in α -terpineol and n-octanol solutions

Sandra Orvalho, Lucie Stikova, Petr Stanovsky, Maria Zednikova, Jiri Vejrazka, Marek Ruzicka

Czech Academy of Sciences, Institute of Chemical Process Fundamentals, Rozvojova 135/1, 165 02 Prague 6 - Suchbátka, Czech Republic

Corresponding author: orvalho@icpf.cas.cz (Sandra Orvalho)

Abstract: This work presents results of an experimental study of the influence of the approach velocity on the coalescence of bubbles in aqueous solutions of n-octanol and α -terpineol. Experiments were performed in a coalescence cell allowing synchronized growth of a pair of bubbles in a liquid. High speed camera imaging was used to characterize the growth of bubbles and their interaction in aqueous solution of different concentrations of surfactants. The coalescence efficiency and contact time till coalescence were determined as a function of the approach velocity between bubbles and the concentration of surfactant. It was found that, for both surfactants, when the approach velocity between bubbles was higher than ~ 1 mm/s, the coalescence efficiency was independent of the approach velocity and that the contact time was independent of the concentration of surfactant. Below ~ 1 mm/s, both the coalescence efficiency and the contact time were the function of surfactant concentration. For the higher velocities, the suppression of coalescence occurred at concentrations similar to the concentration of immobilization of the surface of free rising bubbles.

Keywords: bubble, coalescence, frother, approach velocity, non-ionic surfactant

1. Introduction

Frothers are surface active compounds used in flotation practice to suppress bubble growth due to coalescence (Cho and Laskowski, 2002), to facilitate the formation of three phase contact line and to ensure sufficient stability of the froth (Leja, 1982). The formation of three phase contact line between bubble and ore surface in a froth solution is being subject of increasing interest nowadays (e.g. reviews Ralston et al., 2002; Albijanic et al., 2010; Zawala et al., 2015). Interestingly, it has been shown, using high-speed video, that low concentration of frother decrease the time necessary for bubble attachment, but higher concentrations of frother prolongs the attachment process. With the increase of frother concentration, the bouncing of bubbles from either solid or liquid interface is diminished and the controlling process for coalescence time becomes the thinning of the film between bubbles (Kosior et al., 2013; Kosior et al., 2014). Besides traditional mineral froth flotation, novel applications are being explored, where the frother has a strong effect on the attachment time, e.g. separation of waste plastics (Fujasova-Zednikova et al., 2010; Zhao et al., 2015).

The latter feature of frothers - suppression of coalescence in a gas-liquid-solid mixture is also one of the key ingredients of the flotation process as large bubbles are more prone to break-up and population of small bubbles have a higher probability of collision with ore particles. It is well known that suppression of coalescence can be facilitated by sufficient amount of either surface active organic compounds or inorganic electrolytes (Lessard and Zieminski, 1971; Sagert and Quinn, 1978; Zahradnik et al., 1999). It has been shown recently that thinning of the film between bubbles also depends on other operational variables as the liquid phase viscosity and the mutual approach velocity between bubbles. The viscosity of the liquid phase increases the time necessary for coalescence, following

theory of drainage of thin films, however the viscosity limit for transition to non-coalescent regime depends on the approach velocity between the bubbles' interfaces (Firouzi et al., 2015; Orvalho et al., 2015). Taking the approach velocity between bubbles' interfaces as a simple description of the local hydrodynamic conditions in the various stages of flotation process (formation of particle-bubble assembly, drainage and coarsening of froth) can help to elucidate the role of different frothers on coalescence process at different speeds.

This paper presents results on the influence of the approach velocity between bubbles on their mutual coalescence in n-octanol and α -terpineol solutions. Although the approach velocity range studied in the present work is about one order of magnitude lower than in studies about interactions between bubble-liquid interface or bubble-rigid surface studies (Kosior et al., 2015; Zawala et al., 2015), this study is complementary to them. Moreover, the lower velocity range of the present study can be regarded as similar to the final stage of their experiments, when the bubble bouncing stops and the relevant process is the film thinning between bubble and interface.

2. Material and methods

Each experiment consisted in following evolution of two identical bubbles growing synchronously in an aqueous solution, from two capillaries at a fixed distance of 1 mm (distance measured center-to-center of the capillaries). A high speed camera (Photron SA1.1) equipped with Navitar zoom lens was used to record images from the bubble formation till their contact and coalescence or detachment. The experimental setup is the same as used in previous study on the effect of viscosity on bubble coalescence (Orvalho et al., 2015) and is presented in Figure 1.

The experiments were performed in a small covered box of square cross-section (12×12 cm²) made of glass and stainless steel. Inside, two identical glass capillaries ($L = 42$ cm, 200 μm inner diameter, 360 μm outer diameter, fused silica deactivated tubing from Agilent technologies) were held in the vertical position with the center-center horizontal distance fixed at 1 mm. Each pair of bubbles was formed in an undisturbed liquid. Between experiments, the capillaries were kept bubbling to avoid the liquid from getting into the capillary. Just before each experiment, the bubbling was stopped and the experiment was started with both capillaries filled with air, after inspection of the location of the meniscus. The growth of the bubbles was controlled by a series of pressure drop elements and two pressure regulators (EL-Press Bronkhorst, model no. P-602CV-1H1R, max. 50 kPa and model no. P-602CV-6KOR, max. 150 kPa) connected to a D/A converter (National Instruments PCI-6221) and was PC synchronized with the high speed camera and a set of solenoid valves, by a LabVIEW program.

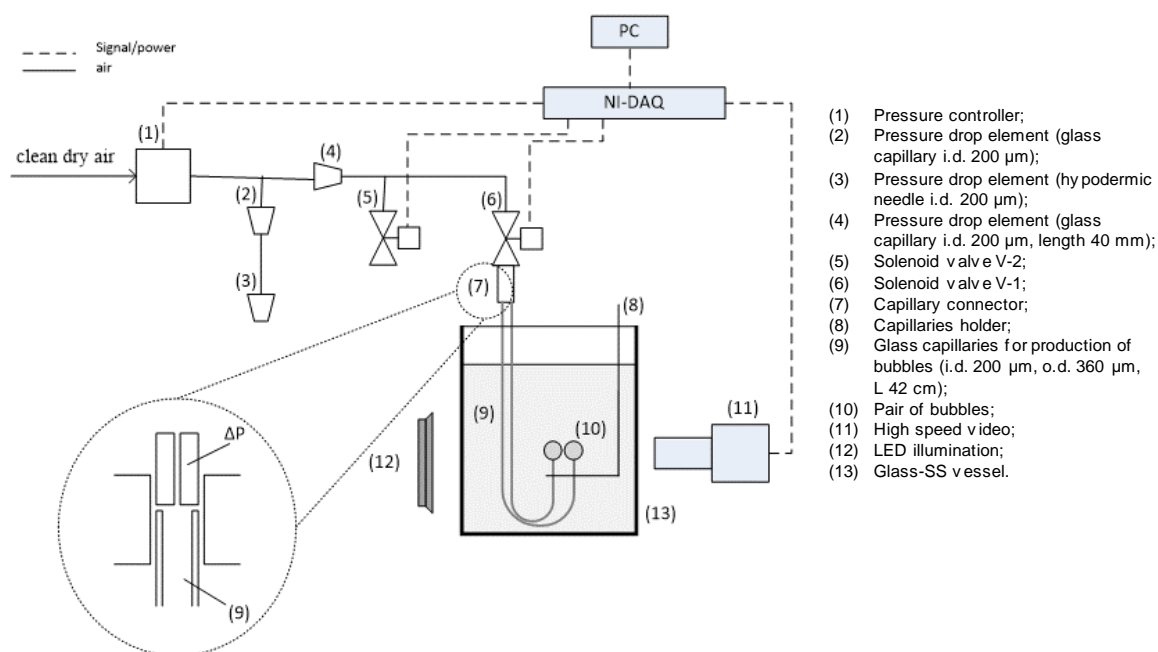


Fig. 1 Experimental setup for study of bubble coalescence

Typical experiments, with or without coalescence, are represented in Fig. 2. Starting with the capillaries filled with gas, the bubble growth and image acquisition is started. Images of the bubbles growing at the capillaries are recorded till the bubbles coalesce or disengage from the capillaries. First analysis of the image sequence gives information about the instant the bubbles appear at the top of capillary, if coalescence occurred or not and when the bubbles merged (coalesced) or disengaged. Posteriori, image processing using Matlab program gives information about the instant the bubbles touch. For each image, the Matlab program identifies the gas-liquid interface and calculates the bubble size assuming axisymmetric geometry of the bubbles. Analyzing the image sequence, the program evaluates the gas flow rate to each bubble (Q) and the approach velocity between them, before touching (V). In the program, the bubbles touch each other when the minimum distance between their interfaces (Δx) is equal or smaller than 1 pixel ($7 \mu\text{m}$). The distance between bubbles at coalescence and disengagement instants are below optical resolution possible with the present camera-lens arrangement and were not measured. The time taken since the bubbles appear at the capillaries till they touch ($\Delta x = 7 \mu\text{m}$) is defined as the inflation time (I). The time taken since the bubbles touch till they coalesce or disengage is the contact time (T). In literature, different authors use different definitions and different names for the contact time, as previously discussed (Orvalho et al., 2015).

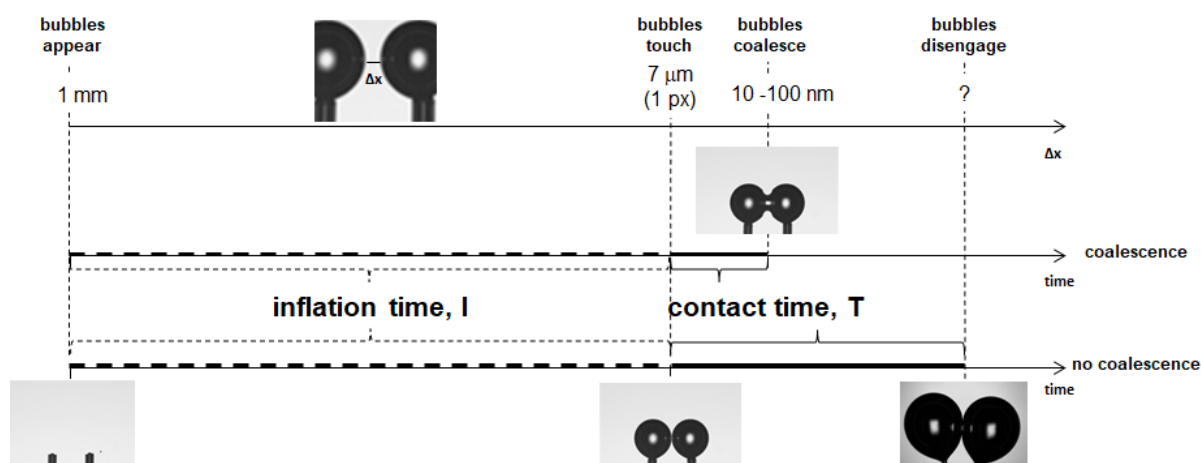


Fig. 2 Definition of evaluated variables from high-speed recording for coalescent/noncoalescent event

The parameters of the present study were: 1) the approach velocity between bubbles, V and 2) the surfactant and its concentration C in the liquid phase. The approach velocity was controlled by the pressure input into the system and evaluated from the image processing results. The pressure into the system, Δp , was set in the interval 3-150 kPa, producing gas flow rates into each bubble in the interval $1 \leq Q \leq 90 \text{ mm}^3\text{s}^{-1}$ giving a range of V of 0.6-40 $\text{mm}\cdot\text{s}^{-1}$. The image acquisition rate was adjusted to the contact time and the bubble growth rate, ranging from 6250-12000 fps for water and 1000-6250 fps for $1.2 \times 10^{-4} \text{ M}$ n-octanol solution. The article presents results on the effect of n-octanol ($1.2 \times 10^{-6} - 1.2 \times 10^{-4} \text{ M}$) and α -terpineol ($6.5 \times 10^{-6} - 6.5 \times 10^{-5} \text{ M}$).

The experiments were done with clean dry air: compressed air from the laboratory lines passed through mechanical filter (Kovofinis CSV 200), condensation drying unit (Donaldson-Ultra filter, Ultratoc-Buran), cloth filter and two activated carbon filters (Ultrafilter, UltraAG-SMF, AG-AK). As liquid phase, aqueous solutions of n-octanol (Sigma-Aldrich, G.R., assay min. 99%) and α -terpineol (SAFC, natural, $\geq 96\%$) were investigated. The surfactants were used without further purification. All the solutions were prepared with ultrapure water: distilled water filtrated by first, an ionic resin bed and after by a carbon activated filter. The temperature of the liquid during experiments was $22.0 \pm 0.3 \text{ }^\circ\text{C}$. All the parts of the experimental setup in contact with the liquid were cleaned with alkali-based cleaner Mucosol and rinsed with ultrapure water several times, prior to the measurements with a new surfactant. The cleanness of the setup was check by blank test of coalescence with ultrapure water, before investigation of the coalescence of bubbles in surfactant solutions, with increasing concentration of surfactant.

3. Results and discussion

Coalescence efficiency measures the actual number of contacted bubbles that coalesced after touching. Figure 1 presents its dependency on the concentration of surfactant C and the effect of the approach velocity V on the inhibition of bubble coalescence. It can be seen that for very small approach velocity, the system is coalescent even at high concentrations. In the case of α -terpineol, the non-coalescent regime was not found in the range of concentrations investigated.

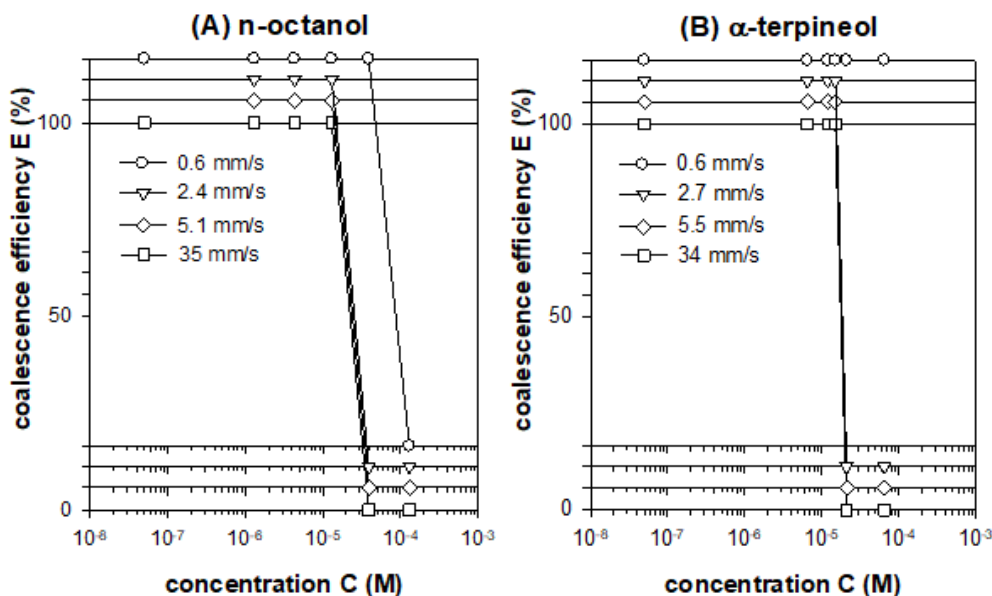


Fig. 3 Effect of concentration of n-octanol (A) and α -terpineol (B) on the coalescence efficiency of bubbles at various approach velocities

In classical studies (Drogaris and Weiland, 1983; Yang and Maa, 1984; Zahradnik et al., 1999) on the effect of surface active additives on bubble coalescence, the transition concentration, C_{trans} , was defined as the concentration at which 50% of the produced bubbles coalesce. These studies were done by observation of the contact between bubbles continuously growing from adjacent nozzles, under different conditions, bubble size at contact, bubbling frequency and approach velocity. Values of C_{trans} in the presence of n-octanol, resumed in Table 1, agree with the interval where inhibition of coalescence was found at $V \geq 2.4$ mm/s, in the present experiments, suggesting that above this value the coalescence efficiency depends only on the concentration of surfactant and not on the size of the bubbles or/and their approach velocity.

Table 1. Values found in literature for C_{trans} in n-octanol solutions

Reference	C_{trans}	Experimental details
Drogaris and Weiland, 1983	2×10^{-5} M	2.5 mm bubbles, unknown bubbling frequency
Yang and Maa, 1984	1.38×10^{-5} M	4.3 mm bubbles, 1 pair/s
Zahradnik et al., 1999	1.3×10^{-5} M	1.8 mm bubbles, 0.75 pair/s

The coalescence efficiency gives little information about the mechanism of bubble coalescence. In the present study, the contact time T was also measured. Figure 4 resumes the contact times measured for the same experiments presented in Fig. 3. At the highest concentration of both n-octanol and α -terpineol, when the coalescence is suppressed, the contact time T is constant for each given approach velocity V . In these cases, T corresponds to the time the bubbles were in contact till they disengaged from the capillaries without coalescing. The constant V corresponds to bubble pairs that grew under identical growth rate conditions. Since all experiments were done with the same capillaries (0.2 mm i.d.) kept at the constant distance, the time necessary for the bubbles to reach the

critical size when the buoyancy overtakes surface forces and the bubbles disengage from the capillaries should be constant for a given V . For lower concentrations of surfactant, when coalescence occurs, then T should be smaller as it is seen for both surfactants. At the lowest approach velocity, the contact time T increases with the increase of concentration C , varying from below 10 ms in distilled water up to 5 s for the highest concentration of surfactant. The increase in n-octanol is smoother than in α -terpineol. Increasing V , both surfactants showed identical behavior: the contact time is either very short, of the same order as coalescence in pure water, when the bubbles coalesce, or very high when the bubbles don't coalesce. In both regimes, the contact time seems to be independent on the concentration, existing a critical concentration above which coalescence is suppressed. In the case of n-octanol, the transition concentration to non-coalescence at the lowest velocities ($V = 0.6$ mm/s) is higher than other velocities. This value $C_{trans} \cong 1 \times 10^{-4}$ M is in accordance with the concentration where Kosior et al. (2014) observed change of thin film stability in the Scheludko-Exerova cell. Measurements in this cell, usually cover approach velocities between interfaces below 1 mm/s (Horn et al., 2011). Kosior and co-workers defined a film as stable when it lasted more than 5 min. The different time scale between our results can be attributed to the fact that in our experiments the time for the thinning of the film between bubbles is limited (bubbles detach from the capillary), while in their type of experiments, both in the thin film cell and in the bubble-free interface experiments, it is unlimited.

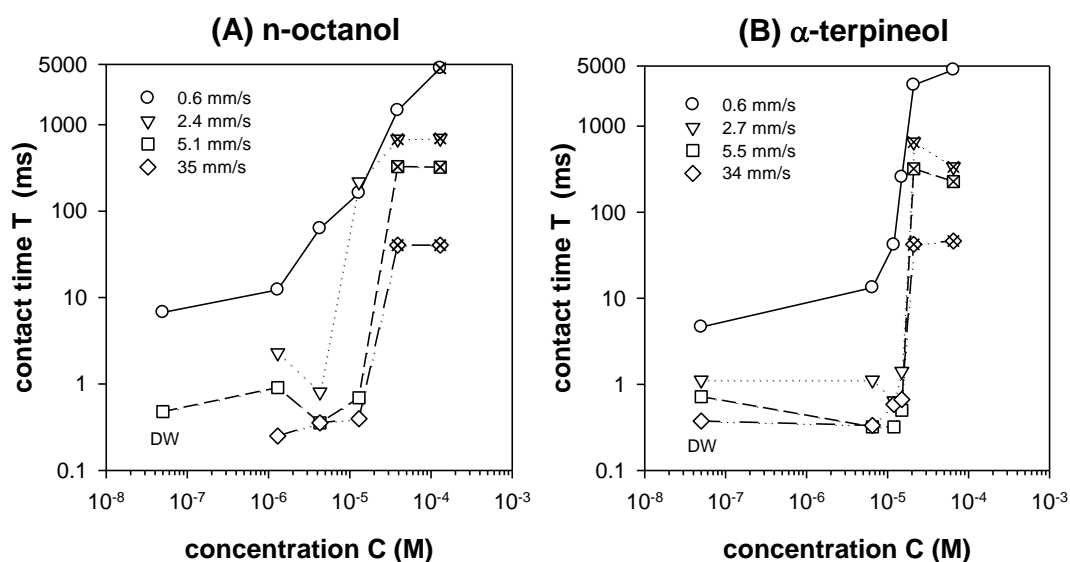


Fig. 4 Effect of concentration of n-octanol (A) and α -terpineol (B) on the contact time between bubbles, till coalescence (open symbols) or disengagement (crossed symbols) at various approach velocities

Table 2. Average approach velocities V and inflation times I for the results in Figs. 3 and 4

n-octanol		α -terpineol	
approach velocity V (mm/s)	inflation time I (s)	approach velocity V (mm/s)	inflation time I (s)
0.56 \pm 0.07	0.65 \pm 0.07	0.59 \pm 0.08	0.68 \pm 0.08
2.4 \pm 0.1	0.132 \pm 0.005	2.7 \pm 0.1	0.12 \pm 0.03
5.1 \pm 0.3	0.068 \pm 0.007	5.5 \pm 0.2	0.060 \pm 0.008
35 \pm 5	0.0141 \pm 0.0005	34 \pm 3	0.015 \pm 0.001

Another aspect of our experiments is that the time the bubbles are exposed to the liquid before they touch, the inflation time I , is not independent of the approach velocity between bubbles V . Table 2 presents the average values of V and corresponding inflation time I . Low approach velocities correspond to slow growing bubbles with longer inflation time I necessary for them to touch, so the bubble's interface is older and has more time to reach full contamination. As the approach velocity increases and inflation time I decreases, the bubbles have less time to reach an equilibrium

concentration. This can explain why the contact time T is sensitive to the concentration of surfactant at low V . Jachimska et al. (2001) calculated the adsorption coverage of bubbles growing in n-octanol solutions. From their data, the 1.5 mm bubble needs more than 3 s to reach equilibrium surface coverage. At the present maximum concentration of 1×10^{-4} M n-octanol, the surface coverage should be less than 10%. All the pairs of bubbles investigated in the present work touched when the bubbles' diameter was 1 mm and it took from 0.01 s to 0.7 s for the bubbles to reach this size, so the surface coverage should be even smaller and very far from equilibrium conditions.

The effect of the approach velocity between bubbles on the contact time till coalescence or disengagement at constant concentration of surfactant is resumed in Fig. 5. Both surfactants studied have similar behavior. In distilled water, the contact time is inversely proportional to the approach velocity up to the point when optical resolution limits the determination of the contact time T and it becomes independent of V . At the maximum concentration of surfactant, the contact time is also inversely proportional to the approach velocity. In these solutions, no coalescence was observed except at the minimum velocity in α -terpineol (note crossed symbols in Fig. 5). As previously referred, in our experiments, if the bubbles don't coalesce, T is limited by the disengagement of the bubbles from the capillaries. At the minimum concentration of surfactant, bubbles coalesce like in water. At $V > 1$ mm/s, the bubbles either coalesce like water or they don't. At $V \cong 0.6$ mm/s, the contact time till coalescence increases with the increase of the surfactant concentrations as already seen in Fig. 4. Two surfactants investigated in this study are both non-ionic and present very similar properties. In both cases, the suppression of coalescence occurs much before any change in the surface tension of the solutions can be measured.

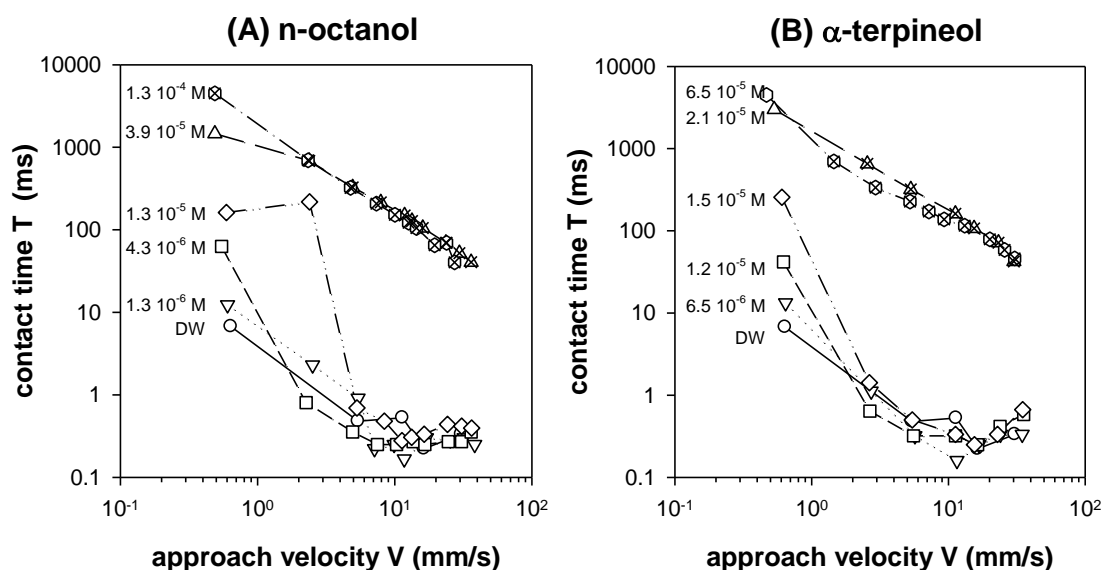


Fig. 5 Effect of approach velocity on the contact time between bubbles, till coalescence (open symbols) or disengagement (crossed symbols) in the presence of n-octanol (A) and α -terpineol (B), at constant concentration of surfactant

It has been observed that immobilization of the interface of bubbles rising in surfactant solutions occurs at surface coverage much lower than the equilibrium value calculated at the time of bubble detachment (Malysa et al., 2011). The minimum surface coverage for retardation is 2% and 6%, for n-octanol and α -terpineol, respectively (Kosior et al., 2013) and it was observed at surfactant concentrations of 3×10^{-5} M for n-octanol and 5×10^{-5} M for α -terpineol. As the bubble size and growth time in these studies is comparable to our experimental conditions, the adsorption relationship for surface coverage can be used (Jachimska et al., 2001). Surprisingly, we observed transition to non-coalescent state at higher approach velocities at almost the same values of surfactant concentrations (3×10^{-5} M for n-octanol and 2×10^{-5} M for α -terpineol) which correspond to the minimum surface coverage for retardation observed in bubble rise studies. We interpret this by following the reasoning that the magnitude of the Marangoni effect causing the bubble drag increase is comparable with that

occurring in the thin film during mutual bubble coalescence, as the change of surface condition at bubbles surface is inherently imposed on the thin film surrounding bubble surface. This retardation effect is also visible in the bouncing of bubbles from hydrophobic surfaces (Kosior et al., 2013), when the drainage time in the presence of surfactant is compared to the case of pure water. At similar concentration, the drainage time rapidly increases in comparison to pure water case with varying slope depending on the surface roughness.

4. Conclusions

Coalescence of 1 mm bubbles in solutions of *n*-octanol and α -terpineol was investigated. Our method allowed characterization of the coalescence efficiency and of the contact time between bubbles produced under controlled conditions (approach velocity bubbles and inflation time till the bubbles touched). Both surfactants showed similar behavior. Around $V = 1$ mm/s, the coalescent behavior of the bubbles changed. Below this value, the contact time till coalescence increased with the increase of concentration of both surfactants and inhibition of coalescence occurred at higher concentrations (in α -terpineol, coalescence occurred in all the range of concentration investigated). Above this value, coalescence was suppressed at a constant value of concentration independently of V and the contact time till coalescence did not depend on the concentration of surfactant. In *n*-octanol, transition to non-coalescence occurred at a concentration very similar to C_{trans} from classical studies of coalescence, obtained under different conditions. For the surfactants investigated, suppressing of coalescence and immobilization of the surface of rising bubbles occurred at similar concentrations suggesting that the immobilization of the interface occurred under identical conditions independently of the velocity, from velocities above 1 mm/s in coalescence of approaching bubbles up to 300 mm/s for bubbles approaching "infinite" surface at bubble's terminal velocity.

Acknowledgements

This work was supported by Czech Science Foundation (project No. 15-15467S).

References

- ALBIJANIC, B., OZDEMIR, O., NGUYEN, A.V., BRADSHAW, D., 2010. *A review of induction and attachment times of wetting thin films between air bubbles and particles and its relevance in the separation of particles by flotation*. *Adv. Colloid Interface Sci.*, 159, 1-21.
- CHO, Y.S., LASKOWSKI, J.S., 2002. *Bubble coalescence and its effect on dynamic foam stability*. *Can. J. Chem. Eng.*, 80, 299-305.
- DROGARIS, G., WEILAND, P., 1983. *Coalescence behaviour of gas bubbles in aqueous solutions of *n*-alcohols and fatty acids*. *Chem. Eng. Sci.*, 38, 1501-1506.
- FIROUZI, M., HOWES, T., NGUYEN, A.V., 2015. *A quantitative review of the transition salt concentration for inhibiting bubble coalescence*. *Adv. Colloid Interface Sci.*, 222, 305-318.
- FUJASOVA-ZEDNIKOVA, M., VOBECKA, L., VEJRAZKA, J., 2010. *Effect of Solid Material and Surfactant Presence on Interactions of Bubbles with Horizontal Solid Surface*. *Can. J Chem Eng.*, 88, 473-481.
- HORN, R.G., DEL CASTILLO, L.A., OHNISHI, S., 2011. *Coalescence map for bubbles in surfactant-free aqueous electrolyte solutions*. *Adv. Colloid Interface Sci.*, 168, 85-92.
- JACHIMSKA, B., WARSZYNSKI, P., MALYSA, K., 2001. *Influence of adsorption kinetics and bubble motion on stability of the foam films formed at *n*-octanol, *n*-hexanol and *n*-butanol solution surface*. *Colloid Surf. A*, 192, 177-193.
- KOSIOR, D., ZAWALA, J., KRASOWSKA, M., MALYSA, K., 2013. *Influence of *n*-octanol and alpha-terpineol on thin film stability and bubble attachment to hydrophobic surface*. *Phys. Chem. Chem. Phys.*, 15, 2586-2595.
- KOSIOR, D., ZAWALA, J., NIECIKOWSKA, A., MALYSA, K., 2015. *Influence of non-ionic and ionic surfactants on kinetics of the bubble attachment to hydrophilic and hydrophobic solids*. *Colloid Surf. A* 470, 333-341.
- KOSIOR, D., ZAWALA, J., TODOROV, R., EXEROWA, D., MALYSA, K., 2014. *Bubble bouncing and stability of liquid films formed under dynamic and static conditions from *n*-octanol solutions*. *Colloids Surf. A*, 460, 391-400.
- LEJA, J., 1982. *Surface Chemistry of Froth Flotation*. Plenum Press, New York.

- LESSARD, R.R., ZIEMINSKI, S.A., 1971. *Bubble Coalescence and Gas Transfer in Aqueous Electrolytic Solutions*. *Ind. Eng. Chem. Fund.*, 10, 260-269.
- MALYSA, K., ZAWALA, J., KRZAN, M., KRASOWSKA, M., 2011. *Bubbles Rising in Solutions; Local and Terminal Velocities, Shape Variations and Collisions with Free Surface*. in: MILLER, R., LIGGIERI, L. (Eds.), *Bubble and Drop Interfaces*. Brill, Leiden, pp. 243-292.
- ORVALHO, S., RUZICKA, M.C., OLIVIERI, G., MARZOCHELLA, A., 2015. *Bubble coalescence: Effect of bubble approach velocity and liquid viscosity*. *Chem. Eng. Sci.*, 134, 205-216.
- RALSTON, J., DUKHIN, S.S., MISHCHUK, N.A., 2002. *Wetting film stability and flotation kinetics*. *Adv. Colloid Interface Sci.*, 95, 145-236.
- SAGERT, N.H., QUINN, M.J., 1978. *The coalescence of gas bubbles in dilute aqueous solutions*. *Chem. Eng. Sci.*, 33, 1087-1095.
- YANG, Y.M., MAA, J.R., 1984. *Bubble coalescence in dilute surfactant solutions*. *J. Colloid Interf. Sci.*, 98, 120-125.
- ZAHRADNIK, J., FIALOVA, M., LINEK, V., 1999. *The effect of surface-active additives on bubble coalescence in aqueous media*. *Chem. Eng. Sci.*, 54, 4757-4766.
- ZAWALA, J., KOSIOR, D., MALYSA, K., 2015. *Formation and influence of the dynamic adsorption layer on kinetics of the rising bubble collisions with solution/gas and solution/solid interfaces*. *Adv. Colloid Interface Sci.*, 222, 765-778.
- ZHAO, Y., LI, Y.P., HUANG, J., LIU, J., WANG, W.K., 2015. *Rebound and attachment involving single bubble and particle in the separation of plastics by froth flotation*. *Sep. and Purif. Technol.*, 144, 123-132.