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# Stability of thin liquid film in bubble-solid adhesion 

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## INTRODUCTION

Interactions between a gas bubble and a solid particle are a key aspect in many processes used in various branches of industry. An example of such a process that has found its widest application in mineral processing is flotation. Flotation is used to selectively separate particles dispersed in a liquid, based on the difference in their surface properties (mainly wettability) using air bubbles. One of the key steps in the flotation process is the attachment of the gas bubble to the surface of the solid by forming a three-phase contact (TPC) at the gas-liquid-solid interface. Effective TPC formation depends on the action of electrostatic and bydrophobic forces. The contribution of hydrophobic forces increases with increasing hydrophobicity of the solid surface, however, despite many published works on this issue (e.g. [1]), the phenomena underlying this process are still not fully known and understood.
Therefore, this study attempts to explain the phenomena underlying the formation of a three-phase contact (TPC) between an air bubble and a glass surface of different wettability, additionally considering the influence of the zeta potential of these surfaces.

## MATERIALS AND METHODS

Microscope slides made of soda lime glass were used as a model solid substrate. The modification of the wettability was carried out using the esterification with $n$-alcohol method. The alcohols with carbon chain lengths from $\mathrm{C}_{3}$ to $C_{10}$ were used. Before the modification the surface was cleaned by immersing for 30 min in a mixture of hydrochloric acid ( $35 \%$ ) and methanol ( $1: 1 \mathrm{v} / \mathrm{v}$ ), and then in concentrated sulphuric acid. Each time, the slide was washed with a copious amount of ultrapure water. After dryig, the glass slide was placed in alcohol, which was heated under a reflux condenser. After an appropriate time (4-6 h), the plate was removed from the alcohol and it was washed with acetone, and then dried at $80^{\circ} \mathrm{C}$.
The degree of hydrophobicity of the modified surface was determined by water contact angle $(\theta)$ measurment. The contact angle was calculated based on the analysis of the shape of a $0.2 \mu \mathrm{l}$ droplet placed on surface using OCA 15EC (Data Physics) goniometer (Fig. 1.).


Fig.1. Images of a water droplet placed on a microscope slide with a modified surface, along with the value of the measured contact angle

The thin-film stability measurements were carried out using a setup for observation of dynamic interactions between a bubble and a surface (Fig. 2.). The setup consists of a high-speed digital camera that is able to record images with a time resolution of 1 ms . Three-phase contact formation time ( $\mathrm{t}_{\mathrm{TPC}}$ ), calculated as a period between the first collision of the bubble with the surface and the rupture of the thin liquid film, was determined by analysing recorded images of bubble-surface interaction.


Fig. 2. Experimental setup for thin liquid film stability determination
The zeta potential of the glass in 1 mM KCl solution was measured as a function of pH using a SurPass 3 electrokinetic zeta potential analyser (Data Physics).

## REFERENCES

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## RESULTS

Based on the results of the glass slides zeta potential measurements (Fig. 3), the pH conditions for TPC formation experiments were determined so as to obtain different potnetial arrangement between inte racting surfaces (Fig. 4).
pH 2


Bubble: positive
pH 5


Surface: isoelectric point
Bubble: negative
pH 4


Surface: positive
Bubble: negative
pH 10


Surface: negative
Bubble: negative

Fig. 3. Zeta potential of glass with different contact angles depending on the pH of the 1 mM KCl solution. Data for an air bubble based on [2].

Fig. 4. Schematic illustration of process conditions with indi rated sign of the zeta potential for solid surface and bubble

For all tested pH conditons, there is a critical contact angle ( $\theta_{\text {crit }}$ ) below which the three-phase contact between the bubble and the glass surface is not formed (Fig. 5) $-\theta_{\text {crit }}=31^{\circ}$ in the case of the $\mathrm{pH} 2-5$ and $\theta_{\text {crit }}=35^{\circ}$ in pH 10.

The time needed for TPC formation decreases as the contact angle (hydrophobicity) of the surface increases. For $\mathrm{pH} 2-5$ the obtained $\mathrm{t}_{\mathrm{TpC}}$ values do not differ significantly from each other. Higher $\mathrm{t}_{\text {TpC }}$ values are obtained when both the bubble and the solid surface have a negative zeta potential ( pH 10 ). It is especially visible in the range of the contact angle of the surface of ca. $35-55^{\circ}$. This indicates a strong influence of repulsive electrostatic interactions. However, as the hydrophobicity of the surface increases, this difference decreases and after exceeding the contact angle of ca. $65^{\circ}$ the $\mathrm{t}_{\text {ThC }}$ values, regardless of the pH , have a similar values.


Fig. 5. Three-phase contact formation time between bubble and solid surface of different wetability
Additionally, the influence of the surface hydrophobicity on the three-phase contact foramtion parameters, such as the angle between the bubble and the surface (Fig. 6), the ratio of the TPC diameter to the bubble diameter (Fig. 7) and the rate of expansion (Fig. 8) were determined.


## CONCLUSION

On the basis of the obtained values of three-phase contact formation time between air bubble and flat solid surface of different hydrophobicity, it can be concluded that there is a minimal contact angle required for bubble adhesion and its value is $31-35^{\circ}$, depending on the pH conditons. With an increase in contact angle, the repulsive electrostatic forces, stabilizing the wetting film and preventing the gas bubble from adhering to the solid surface, become insufficient to overcome the increasing attractive hydrophobic interactions. In the case of a surface with contact angle exceeding $60^{\circ}$, the nature of electrostatic interactions between the surfaces practically no longer affects the time of contact formation.
The tests under various pH conditions also show that the process of TPC expansion is influenced only by the wettability of the surface, and not by electrostatic interactions.

