

## Pulsating drop technique to characterize surfactant behavior in flotation process

This application note describes how Attension Theta pulsating drop module, PD200, can be used to study surfactant behavior in flotation process.

### Introduction

Flotation is widely used primary concentration process especially utilized in the mineral processing industry. It is based on the interfacial chemistry of mineral particles in solution. In addition to mineral processing, flotation is also used in waste water treatment, extraction of bitumen from oil sand and paper deinking.

The principle of flotation process is simple: In the flotation tank, fine bubbles are dispersed in the pulp containing finely grounded ore particles. Depending on hydrophobicity of the ore particles, they are able to attach to the air bubbles. Thus, valuable ore is lifted to the top of the tank from where they are skimmed off, while gangue minerals stay in the pulp. The dispersed air bubbles play a key role in the process. Their properties are strongly influenced by the composition of the fluid medium that consists of water and flotation reagents, such as frothers, collectors, depressants, etc. Of all these reagents, frothers are surface active substances that effect on formation and behavior of the air bubbles. The frother molecules adsorb on the bubble surface creating an adsorption layer. During the adsorption the surface tension [ $\gamma$ ] decreases until it reaches an equilibrium value. Under dynamic conditions the kinetics of adsorption and desorption of surfactants to and from solution have a major effect on the behavior of bubbles. Understanding the rheological properties of the adsorbed layers is important for characterization of commercial surfactants.

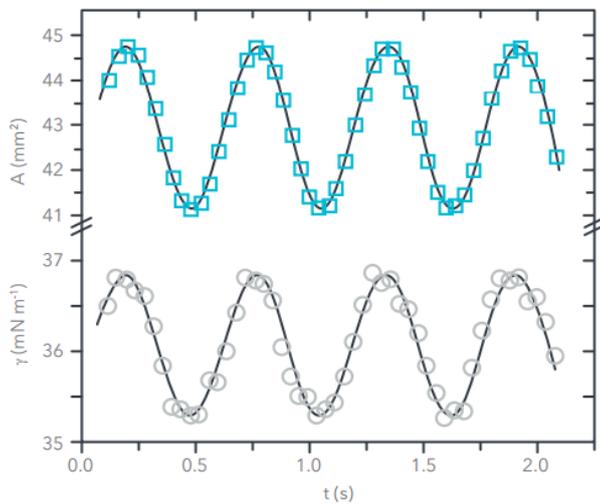
The dilatation rheology is an unique tool suitable to investigate equilibrium and dynamic properties of interfacial layers. Surface elasticity [ $E$ ] of the interface defined by Gibbs:

$$E = \frac{d \gamma}{d \ln A} \quad (1)$$



Theta Optical Tensiometer with with pd200 module

where  $A$  is the surface area. Only for pure elastic interfaces, the dynamic interfacial tension response [ $\gamma(t)$ ] follows immediately the area change [ $A(t)$ ] without any phase lag (Fig 1). However, in general the interfacial tension follows the area change with a certain delay due to the various relaxation processes within the interfacial layer, and between the interface and the adjacent bulk system [1].



[Figure 1]: Response of the surface tension and bubble area for a sinusoidal perturbation of a pendant drop [2].

To describe this surface property the complex surface dilatational modulus [ $E^*$ ] [2] can be written as

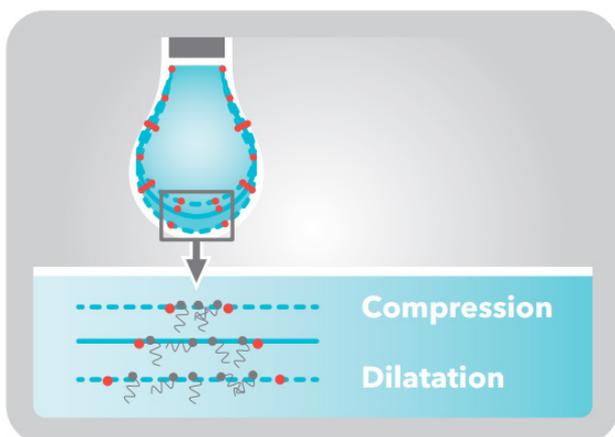
$$E^* = E' + i \cdot E'' \quad (2)$$

where  $E'$  is called to storage modulus which is obtained as the pure dilatational elasticity and  $E''$  is loss modulus and is proportional to the viscous contribution [2]

$$E'' = \omega \eta_d \quad (3)$$

where  $\eta_d$  is the surface dilatational viscosity and  $\omega$  the circular frequency.

The capillary wave and oscillating bubble techniques were the first two methods developed to measure surface dilatational elasticity. The bubble oscillation method developed by Lunkenheimer and Kretzschmar [4] uses harmonic interfacial disturbance to measure the surface dilatational elasticity. A small bubble is formed at the end of a capillary tip and a membrane is used to create harmonic oscillation (Figure 2). This technique allows to measurement of the surface dilatational elasticity at relatively high frequencies.



[Figure 2]: Adsorption kinetic of surfactant on a pulsating bubble.

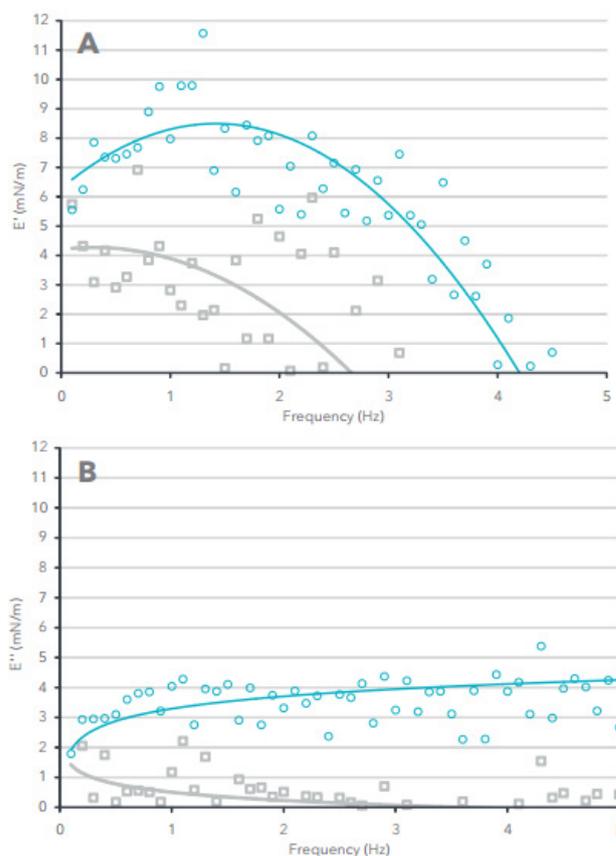
The modified pendant drop technique [5] works on the same principle as the oscillation bubble method. The high resolution and excellent accuracy ( $\pm 0.1$  mN/m) provides a useful tool for studies of dynamic of adsorption layers. The method can be applied to liquid-gas as well as liquid-liquid interfaces. [6].

The Pulsating Drop Module provided by Attension is a compact, optional module to Theta optical tensiometer to measure surface dilatational elasticity based on the modified pendant drop technique.

### Case study: Investigation of dynamic properties of air-water interfaces in presence of different surfactants

During the flotation process different frothers affect the recovery of valuable minerals most probably by changing the interfacial rheological properties of bubble surfaces. The property of interfacial layer could effect on bubble size and/or attachment of particle to bubble surface. In this study the Attension Pulsation Drop Module was used to investigate the effect of two well-known commercial frothers, Nasfroth 240 (NF240) and Dowfroth 250 (DF250), on dilatational elasticity and viscosity of the bubbles surface.

Even though the concentrations of the two solutions are identical (25ppm) the result shows different surface properties as it can be seen on Figure 3. The air/water interface created in presence of DF250 shows high elasticity and viscosity compare to that created in NF240 solution. The difference could be due to the different chemical structure and molecular conformations of the two surfactants.



[Figure 3]: Dependence of dilatational elasticity (A) and dilatational viscosity (B) from increasing oscillation frequency of water droplet in presence of 25ppm NF 240 (o) and 25ppm of DF 250 (o).

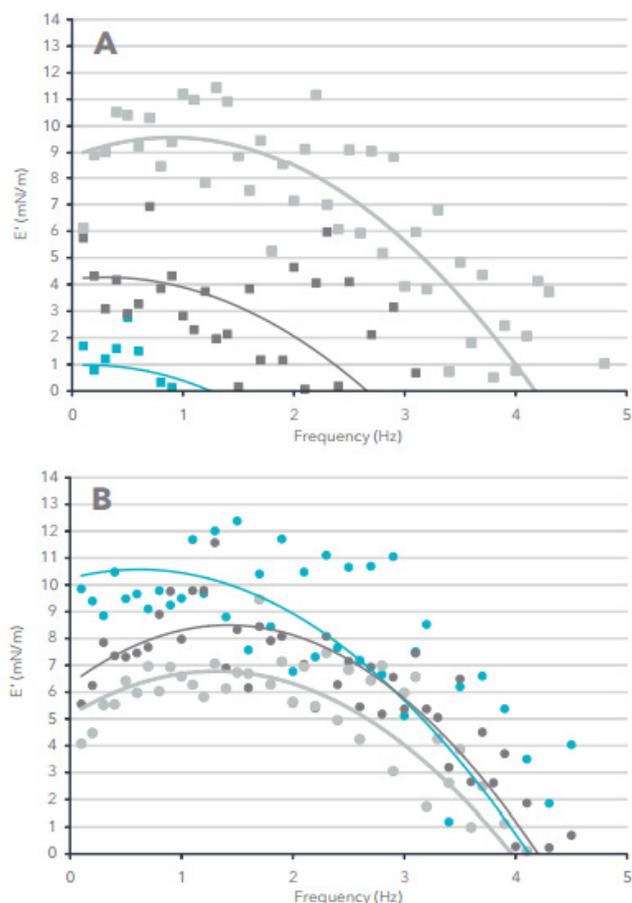
Surfactants are widely used in flotation to generate smaller bubbles (ca. 0.5-3 mm) and to foster froth phase and stabilize it. Even though small bubbles play a major role in flotation performance, little is known about the effect of frothers on their formation.

Cho and Laskowski [7] studied the effect of frothers on bubble size. They found that with increasing frother concentration the size of the bubbles decrease due to the resistance of bubbles to coalescence. The ability of the frothers to prevent coalescence depends on not just the concentration, but also the type of the surfactant. Frothers have a particular concentration (critical coalescence concentration; CCC) where the coalescence of the bubbles is completely prevented.

The dilatational elasticity of air-water interface was studied with Attension Pulsation Drop Module in presence of NF240 and DF250 frothers. The aim was to investigate how the surface properties are changed when the concentration of the frothers was increased from below the CCC point to above the CCC point. The increasing concentration of surfactant causes different effect on surface elasticity in presence of the two different types of frothers as it can be seen on Figure 4. In NF240 solution the increasing concentration causes higher elasticity due to the decrease of surface tension. However in presence of DF250 with increasing frother concentration the elasticity of the interface decreases. This phenomenon could be explained with the faster molecule exchange. The higher the concentration, the faster the exchange and the lower the elasticity.

## Conclusions

The pulsation drop technique is an accurate technique to investigate the rheological properties of interfaces with relatively high frequencies. The dilatation rheology is an unique tool to characterize the elasticity of air-liquid or liquid-liquid interfaces under dynamic condition. The dynamic surface elasticity is able to demonstrate adsorption kinetics via pure dilatational elasticity and dilatational viscosity results. This technique is very valuable for characterizing commercial surfactants used in flotation process.



**[Figure 4]:** Change of dilatational elasticity with increasing oscillation frequency in presence of increasing concentration of NF 240 (A) and DF 250 (B). The used concentrations are 8ppm (blue), 25ppm (dark grey) and 100ppm (light grey).

## References:

- [1] R. Miller, J.K. Ferri, A. Javadi, J. Krägel, N. Mucic and R. Wüstneck, *Colloid Polym Sci* (2010) 288: 937
- [2] R. Myrvold and F.K. Hansen, *J Colloid Interface Sci* (1998) 207: 97
- [3] R. Miller and L. Liggieri, "Progress in colloid and interface science: Interfacial rheology", vol 1. Brill, Leiden (2009)
- [4] K. Lunkenheimer and G. Kretzschmar, *Z. Phys. Chem.*, (1975) 256: 593
- [5] R. Miller, Z. Policova, R. Sedev, and A.W. Neumann, *Colloids & Surfaces*, (1993) 76: 179
- [6] S.S. Dukhin, G. Kretzschmar and R. Miller, "Dynamic of Adsorption at Liquid Interfaces" Elsevier, Amsterdam (1995)
- [7] Y.S. Cho, J.S. Laskowski, *Int J Mineral Process* (2002) 64: 69