

## BUBBLEDROP ANALYZER

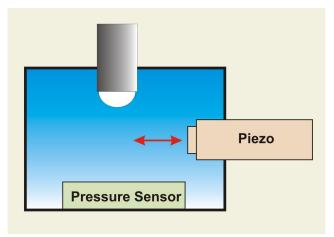


THE BUBBLEDROP ANALYZER of OPTREL GBR is a powerful surface analytical tool for Colloid and Interface Science. It measures the complex surface dilatational modulus E of aqueous surfactant solution in a frequency range of 1 to 600 Hz. The extension to the mid frequency range is decisive for the investigation of soluble surfactants as the molecular exchange processes between adsorbed and dissolved amphiphiles contribute at higher frequencies significantly to the E-modulus.

The real and the imaginary part of the *E*-modulus are directly and precisely measured. The imaginary part of the modulus gives access to the intrinsic surface dilatational viscosity  $\kappa$ . This parameter is decisive for the formation of a foam lamellas as well as for high speed coating processes or micro fluidics.

## Principle of the measurement

The measurement is based on the oscillating bubble technique as outlined in the following cross-sectional view of the cell:

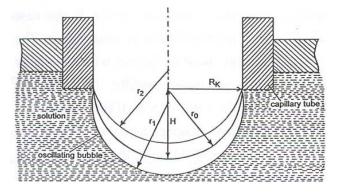


The device consists of a metal chamber, a capillary with an inner diameter of about 0.3 mm, a pressure sensor at the bottom of the cell and an imaging system. The chamber is filled with an aqueous surfactant solution such that an air bubble is formed at the tip of the capillary. The bubble is visualized by a video zoom imaging system and automatically adjusted to a half sphere geometry which simplifies the underlying equations.

The bubble is then forced in a well defined oscillation by the piezo. The change of the bubble size modifies the pressure within the chamber which is monitored by a piezoresistive pressure sensor. The pressure response is sinusoidal with the following contributions:

$$\Delta p = -\frac{2}{r_0} \Delta \gamma + 2\frac{\gamma}{r_0^2} \Delta r + H(f) \tag{1}$$

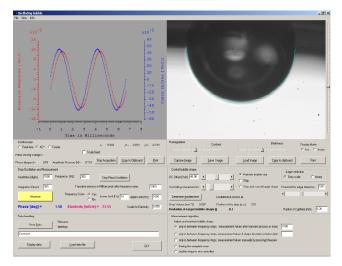
 $\Delta r$  describes the deviation of the bubble radius r from the halfsphere  $r_o$ ,  $\Delta \gamma$  denotes the change in the interfacial tension  $\gamma$  and H(f) captures the influence of the hydrodynamics, bulk viscosity and inertia. The frequency dependent hydrodynamic term H(f) contributes at frequencies above 200 Hz. In principle H(f) can be estimated by explicit calculations, but a sound alternative are calibration measurements using a purely elastic surface layer such as decanoic acid.



The system is operated by a computer and a frequency scan requires only a couple of minutes. The piezo motion is controlled by an AD-DA converter which processes also the amplified signal of the pressure sensor. The amplitude of the pressure response and the phase-shift between piezo oscillation and pressure response are evaluated via a phase sensitive lockin detection scheme. The amplitude of the pressure response is proportional to the absolute value of the complex surface dilatational modulus E, while the phase-shift yields the imaginary part of the modulus, in other words the surface viscosity. Bubble and capillary are imaged by a video zoom imaging module, digitized and processed in a personal computer. The video system is crucial for maintaining the bubble size and to compensate thermal drifts in the chamber.

The implemented design gives access to the frequency range of 1-600 Hz as a major difference to all other commercial drop devices which rely on the analysis of the drop contour. The frequency range around 100-400 Hz is of particular importance for aqueous surfactant solution. The design of the cell suppresses many unwanted features such as Maragoni flow. Investigations with a high speed camera reveal that the three phase contact line at the capillary remains constant at all frequencies. Furthermore the studies reveal that the drop oscillates in the zero order mode even at frequencies around 600 Hz.

The instrument is fully computer controlled and comes with software for data analysis.

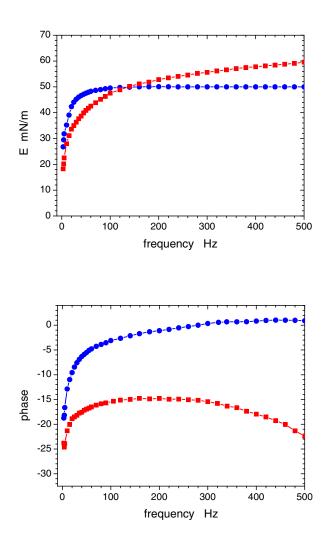


Several algorithms are implemented to meet the demands of your samples. The user has online control of all parameters. The blue line in the screen dump reflects the piezo position, the red line is the pressure response. Both are truly harmonic signals with a defined phase relation. These signals are processed and evaluated. The complex E modulus has two components:

$$E(f,c) = E(\Gamma) + i2\pi f\kappa \tag{2}$$

The first term accounts for the changes in the surface composition while the second term accounts for the frequency f dependent contribution of the surface dilatational viscosity  $\kappa$  to the *E*-modulus. According to the Lucassen-van den Tempel-Hansen model the compositional term levels off into a plateau at higher frequencies. Under these conditions the adsorption layer of the soluble surfactant behaves as a Langmuir layer of an insoluble amphiphile. The second term increases in a linear fashion with the frequency. Both combined contributions reflect the frequency dependence of the modulus.

The next figure shows the magnitude of the surface dilatational modulus for the C12-DMP at a concentration of  $4.0 \cdot 10^{-3}$  mol/l just below the cmc. The magnitude of the modulus increases at higher frequencies in a linear fashion. This feature is typical for a surface visco-elastic layer. The corresponding phase measurements yield a large phaseshift between piezo and pressure response at higher frequencies, a feature which clearly indicates for a surface viscosity.



The picture changes completely at lower bulk concentration of the very same surfactant. The corresponding measurements are also illustrated in the figure. The magnitude of the |E| -modulus levels off in a plateau at higher frequencies as predicted by the Lucassen -van den Temple model. The corresponding phase vanishes at higher frequencies.

THE BUBBLEDROP ANALYZER of OPTREL GBR measures a fundamental system parameter, the complex surface dilatational modulus. This parameter is decisive in the context of foaming but also for other technological processes such as in the new field of micro fluidics where smaller volumes are manipulated or classical high speed coating processes in the photographic industry. The system has the potential to establish a new standard technique in colloidal laboratories.

## Further reading:

P. Koelsch, H. Motschmann, *Langmuir*, **2005**, *21*, 6265-6269.