

Stability and Structure of Interfaces in Foams and Emulsions

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ABSTRACT

Understanding the properties of adsorbed films at air-liquid or liquid-liquid interfaces is important for formulating stable emulsions and foams in the food, cosmetic, pharmaceutical and coating industries. Adsorbed molecular layers can be studied by measuring their viscoelastic properties. Dynamic rheological experiments are capable of separating the storage (elastic) and loss (viscous) modulus of complex rheological behaviour. In this abstract two methods for the study of interfacial rheology are presented; oscillating drop (dilatational) and interfacial shear rheometry (shear).

INTRODUCTION

Emulsion and foam stability, bubble and micelle formation, breakage and fusion and interfacial reactions are largely affected by the rheological properties of the interface. Just as rheology is the study of flow in bulk fluids, interfacial rheology is the study of flow properties of liquid interfaces. These flow properties are important for many products and industries which require optimum composition for their performance and shelf life^{1,2}.

The structure and dynamics of molecules adsorbed at fluid/fluid interfaces can be studied using both interfacial shear and dilatational deformation³. For interfacial dilatational rheology, pulsating drop method can be utilized. The principle of oscillating

drop method is presented in Fig. 1. It is based on the pendant drop technique where image of a hanging drop is taken and the Young-Laplace equation is fitting around the drop shape. In principle, the volume of the drop, containing surface active molecules, is oscillated with the known frequency. The rheological properties of adsorption layers are expressed by the relationship between the variation of the interfacial tension, from its initial value, and the expansion (or contraction) of the surface area. Dilatational viscoelastic modulus, E can be expressed by Eq.1.

$$E = \frac{\Delta\gamma}{\Delta A/A_0} = E_0 + i\omega\eta \quad (1)$$

The dilatational modulus E is then a frequency dependent complex quantity, where the real part, $E' = E_0$, is the dilatational elasticity and the imaginary part, $E'' = \omega\eta_d$, is directly linked to dilatational viscosity.

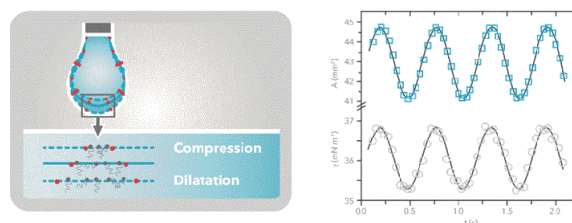


Figure 1. Operation principle of the pulsating drop method.

For measuring shear rheological properties at interfaces, the interfacial shear rheometer provides the opportunity to measure very weak moduli as a function of surface pressure. In the set-up, a magnetised probe is moved at air-water or oil-water interface using a magnetic field created by a Helmholtz coil. The probe movement is recorded optically from above. The complex surface modulus is calculated from the strain and signal phase shift and can be divided into elastic and viscous shear properties of the thin film according to Eq. 2.

$$G(\omega) = \frac{\sigma_s}{\gamma_0} e^{i\delta(\omega)} \quad (2)$$

The modulus can be further divided into the elastic shear modulus G' and viscous shear modulus G'' . The flow of the magnetized probe in the measurement is depicted in Fig 2.

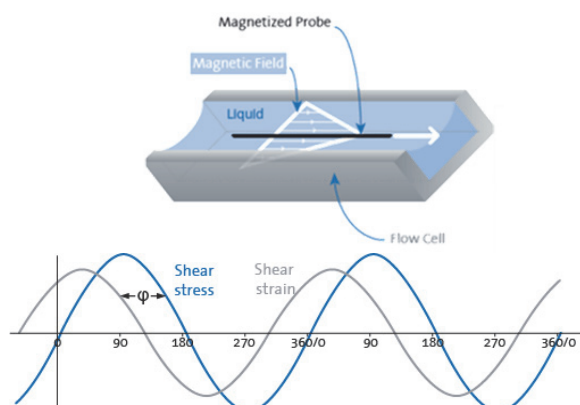


Figure 2. Operation principle of the interfacial shear rheometer.

In this study, results on measuring the viscoelastic properties and the adsorption and network formation of adsorbents to interfaces are presented. Two different examples show the measurements done with the pulsating drop and interfacial shear rheometer. In the interfacial shear rheology study, the phase behaviour of an insoluble monolayer is correlated with shear rheological data. It also demonstrates how precise control of surface pressure during a

measurement makes it possible to model natural systems like cell membranes. In the pulsating drop measurement example, the effect of the number of EO-groups on the surface properties of non-ionic surfactants has been studied.

EXPERIMENTAL

For the interfacial shear rheometer studies, a Langmuir monolayer of 1-eicosanol was created by spreading 80 μ L of 1mg/ml chloroform solution onto a distilled water surface in a Langmuir Trough. An ultra-light glass capillary ISR probe was used in the measurements, and a strain of 30 μ m (approximately 3%) was used in all the experiments.

With the pulsating drop method the adsorption and surface rheology properties of two technical-grade non-ionic surfactants based on C10-Guerbet alcohol differing in the number of EO groups were studied. Two frequencies; 0.02 and 0.5 Hz were used for the measurements. Concentrations from 2.44 mmol/l to 0.24 mmol/l were studied.

RESULTS

Surface storage (G') and loss modulus (G'') obtained from the single frequency experiment are shown in Fig 3. The G'' shows a maximum when surface pressure is approximately 6 mN/m. The monolayer shows highly viscous behavior at low surface pressures (below phase transition at 15 mN/m). As surface pressure increases, the monolayer viscosity decreases until phase transition. After a phase transition, viscosity remains constant.

Both the elastic (G') and viscous modulus (G'') remain constant when the surface pressure reaches approximately 15 mN/m. The surface pressure value corresponds to a phase transition in the packing of the eicosanol monolayer from tilted-liquid to liquid-untitled phase (Fig 4). After the phase transition, the film retains some viscous properties while the elasticity is practically zero (Fig 1). This is in

accordance with similar experiments in literature⁴. At surface pressure 5 mN/m the eicosanol alkyl chains are tilted, and some are parallel to the interface. At 30 mN/m surface pressure all the chains are practically standing upright and there is no measurable elasticity in the film at any frequencies.

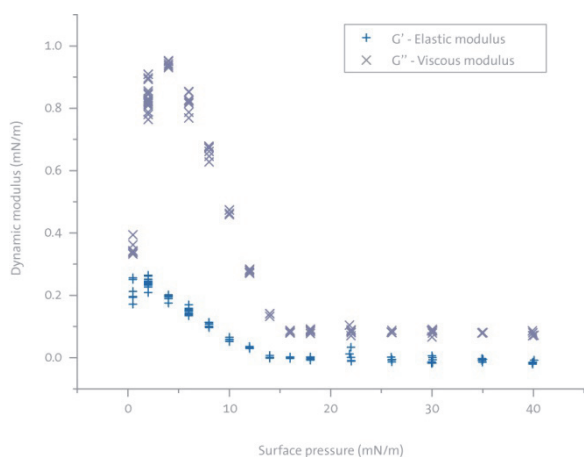


Figure 3. Surface storage and loss moduli for eicosanol as a function of surface pressure.

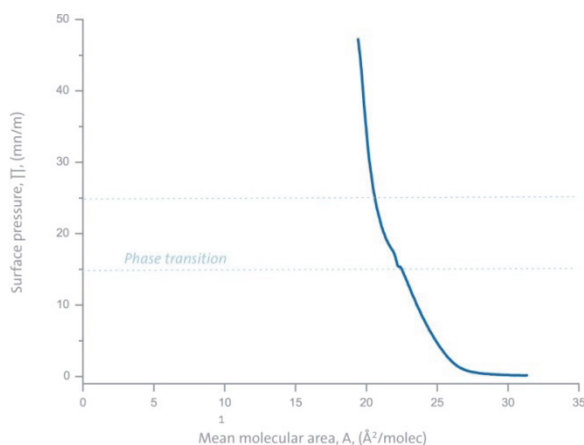


Figure 4. Langmuir isotherm for eicosanol.

Surface dilatational elasticity (storage) and viscosity (loss) modulus as a function of surfactant concentration and frequency are presented for two non-ionic surfactants in Fig 5.

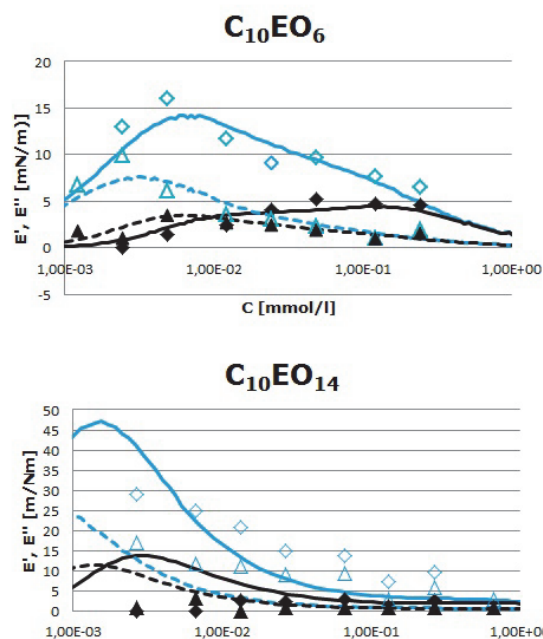


Figure 5. Storage (E' , open symbols) and loss (E'' , close symbols), moduli as a function of surfactant bulk concentration at two frequencies (0.02 Hz – triangles) and (0.5 Hz – diamonds) for $C_{10}EO_6$ and $C_{10}EO_{14}$ surfactants. Solid and dash lines are the best fits of the experimental data to the diffusion model.

From Fig 5. it can be seen that the measured data from the $C_{10}EO_6$ surfactant fits well on the diffusion controlled model whereas the larger $C_{10}EO_{14}$ shows a surface behaviour closer to that of polymeric surfactants. Comparing the dilatational elasticity and viscosity of both surfactants indicates that elasticity is increased by increasing the number of EO groups⁵. Elasticity of the adsorbed surfactant film is related to foam and emulsion stability and therefore $C_{10}EO_{14}$ is likely to form more stable layers against coalescence than shorter $C_{10}EO_6$ surfactant. However, foam formation is will be enhanced by using the smaller molecule due to higher diffusivity.

CONCLUSIONS

The interfacial shear rheometer shows excellent sensitivity, making it capable to measure viscoelastic properties of Langmuir

films and monolayers. It extends the interfacial rheology measurements from not only studying self-absorption of macromolecules but also to study Langmuir monolayers of surface active compounds.

Pulsating drop module offers a relatively fast measurement method for the study of adsorbed interfacial layers. With the method it is possible to gain information on the behaviour of surfactants and find the most suitable surfactant to stabilize foams and emulsions.

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