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KSV NIMA [Application Note] 6

Interfacial rheology of monolayers at the air-water interface

This application note illustrates how the KSV NIMA Interfacial Shear Rheometer can be used to measure viscoelastic properties of Langmuir films and monolayers.

Introduction

Rheology is a branch of science studying the flow of materials. Interfacial rheology concerns the unique two dimensional systems formed between two immiscible phases like liquid and gas or liquid and liquid. The stability of interface depends a lot on the viscoelastic properties of the interface, which makes it a crucial aspect for many industries where foams, emulsions and dispersions are used such as in pharmaceuticals, foods, beverages, cosmetics and coatings.

Interfacial rheology is a challenging field of research because the magnitude of forces in the interface is really small. Rotating ring and bicone methods have been developed, but they have been demonstrated to work only with macromolecular compounds at the interfaces. The KSV NIMA Interfacial Shear Rheometer (ISR) utilizes a small magnetic probe which is moved with an oscillating magnetic field. The method reduces the inertia and enhances the sensitivity of the probe compared to the rotating ring method and makes it possible to measure low molecular weight surface active compounds.

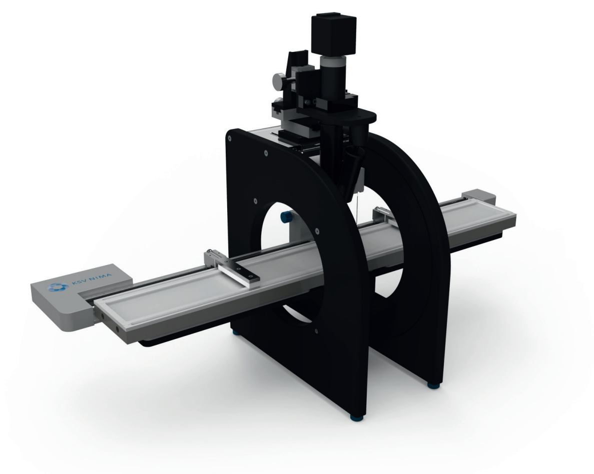
In dynamic rheological experiments three variables are measured: applied stress (σ), strain (γ) and phase shift (δ) between the stress and strain oscillation. Dynamic viscoelastic modulus G* is obtained as a function of oscillation frequency from the measurement, and it can be separated into two components, elastic (or storage) modulus G' and viscous (or loss) modulus G".

$$G^*(\omega) = \frac{\sigma}{\gamma_0} e^{i\delta(\omega)} = G'(\omega) + iG''(\omega)$$

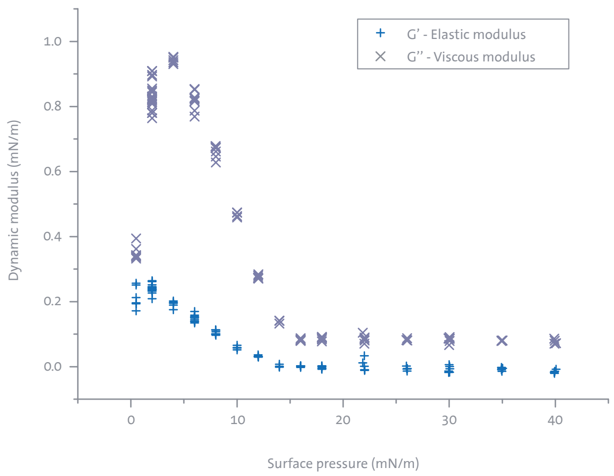
Materials and methods

A Langmuir monolayer of 1-eicosanol was created by spreading 80 µL of a 1 mg/ml chloroform solution onto a distilled water surface using a KSV NIMA ISR Langmuir Trough. An ultra-light glass capillary ISR probe was used in the measurements, and a strain of 30 µm (approximately 3%) was used in all the experiments.

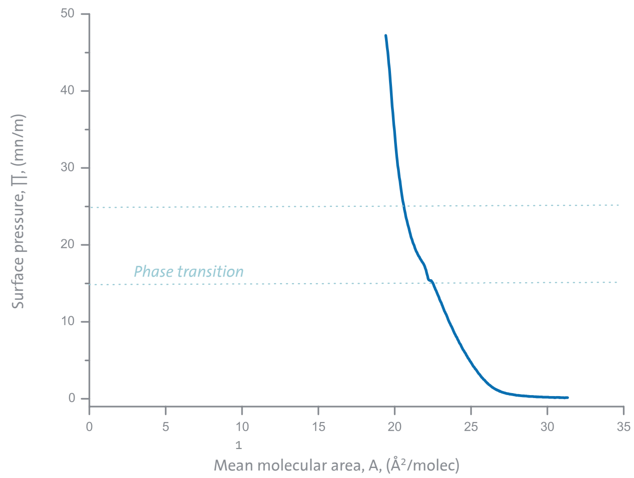
Two different types of experiments were performed. Dynamic single frequency experiments as a function of surface pressure were performed with an oscillation frequency of 0.2 Hz. Frequency sweep experiments as a function of oscillation frequency were performed from two different surface pressures, 5 mN/m and 30 mN/m.



KSV NIMA ISR with KSV NIMA Langmuir Trough



[Figure 1]: Surface storage and loss moduli for eicosanol as a function of surface pressure.



[Figure 2]: Isotherm for eicosanol.

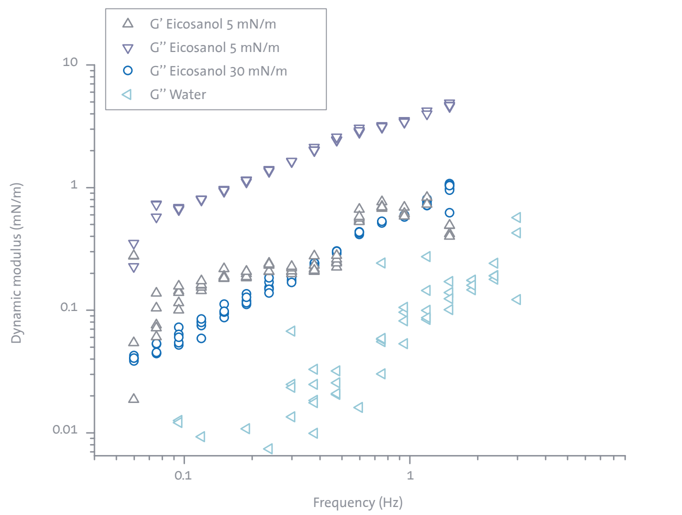
Results and discussions

Surface storage (G') and loss modulus (G") obtained from the single frequency experiment are shown in Figure 1. 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 phase transition, viscosity remains constant.

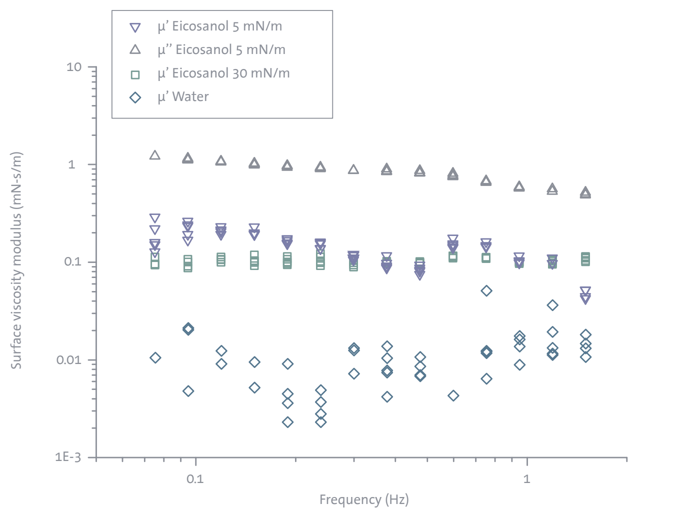
Both the elastic (G') and viscous modulus (G") remain constant when the surface pressure reaches approximately 15 mN/m. The surface pressure value corresponds to a phase transition in the packing of the eicosanol monolayer from tilted-liquid to liquid-untilted phase (Figure 2). After the phase transition, the film retains some viscous properties while the elasticity is practically zero (Figure 1). This is in accordance with similar experiments in literature done with home-built equipment. [1]

The G' and G" values are shown in Figure 3 as a function of frequency for eicosanol at 5 mN/m, 30 mN/m pressure and for pure water. At high surface pressure (30 mN/m) only the G" is measured (frequency dependent) showing that the monolayer has purely viscous properties. The frequency dependent transition at 0.5 Hz in the monolayer at 5 mN/m surface pressure is clearly observed in surface storage (G'). Shear rate –corrected surface modulus (μ' = G"/δ and μ" = G'/δ) is shown in Figure 4 where δ is the phase difference between strain and stress. The graph shows that the monolayer has slight shear-thinning at 5 mN/m but not at 30 mN/m surface pressure.

At surface pressure 5 mN/m the eicosanol alkyl chains are tilted, and some are parallel to the interface. The probe shearing at the interface bends the alkyl chains towards the movement and above the phase transition frequency the chains do not have time to relax to the new conformation. This would explain higher elasticity at higher frequencies. 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.



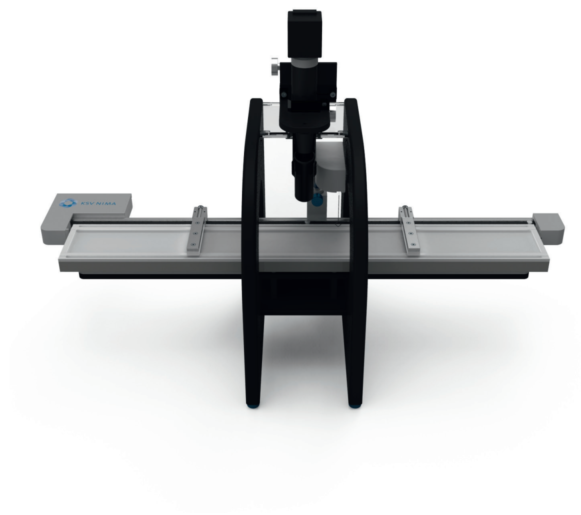
[Figure 3]: Frequency dependence of the dynamic moduli and complex viscosity for eicosanol at 5 mN/m and 30 mN/m. G' for eicosanol at 30 mN/m and water is not seen in the figure.



[Figure 4]: Shear rate - corrected surface modulus as a function of frequency for eicosanol at 5 mN/m, 30 mN/m pressure and for pure water. μ" for eicosanol at 30 mN/m and water is not seen in the figure.

Conclusions

The KSV NIMA 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. This makes it possible to study viscoelastic properties of emulgators that are not polymeric. The precise control of surface pressure during the measurement makes it also capable to model natural systems like cell membranes enabling viscoelastic change measurements at the membrane level.



References:

[1] Brooks, C.F. et al. Langmuir 1999, 15, 2450-2459

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