

Measuring the Rheological Properties of Ultrathin Films at the Water-Air and Water-Oil Interface by Using a Novel Double Wall Ring (DWR) Geometry

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ABSTRACT

The new double-wall ring (DWR) geometry is used on a range of interfacial thin films, at both the water-air and water-oil interface. Results on surfactants show the DWR is able to measure viscous as well as viscoelastic interfaces in both continuous shear and oscillatory experiments.

INTRODUCTION

The interfacial shear rheology of thin layers at liquid-liquid or liquid-gas interfaces has been a subject of increased interest for many years. The research has been motivated by the need to understand the effects of particles, surfactants or proteins at these interfaces in a variety of applications such as structured food products, biomedical, enhanced oil recovery and many more. Interfacial shear rheometry aims at measuring the linear and nonlinear rheological properties of an interfacial layer i.e. the adsorbed monomolecular film at a liquid-liquid or liquid-gas interface.

Recently, several devices that could be used to study the interfacial rheological properties and can be used in conjunction with rotational rheometers have been suggested. The most common ones are the bi-cone/disc¹ and the Du Noüy ring. These devices are robust and relatively easy to use,

but they have their limitations. The bi-cone and disc geometries can be used for viscous and elastic interfaces, but the sensitivity is limited because of the large area in contact with the bulk fluid, relative to the perimeter in contact with the interface.

As the contributions of the viscous drag exerted by the bulk liquid(s) and the viscoelastic response coming from the interface need to be separated, it is advantageous to reduce the amount of surface in contact with the surrounding phases. The Du Noüy ring, originally developed for surface tension measurements, has been suggested as a suitable alternative that meets this requirement, but its use is hindered by some fundamental limitations. For example the round cross-section of the ring is also far from ideal for pinning the interface, hence the interface can easily slip over the ring, avoiding coupling.

THE DOUBLE WALL RING (DWR)

The double wall ring (DWR) geometry in Fig. 1 is the result of combining the best features of both, the Du Noüy ring and the bi-cone.

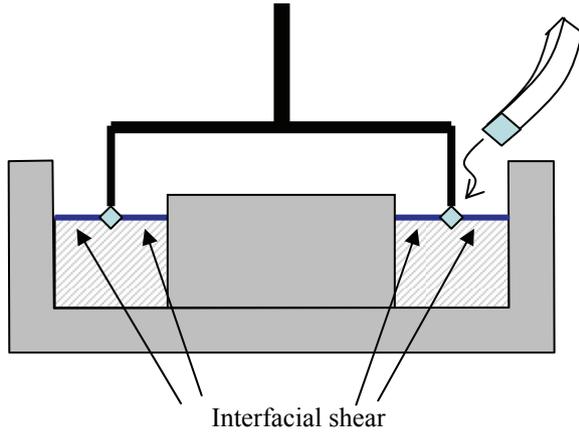


Figure 1. Schematic of the DWR configuration.

The round wire shape of the actual Du Noüy ring has been replaced with a square cross-section to improve the ability to pin the interface. The diameter of the ring has been enlarged to increase the torque i.e. sensitivity. Also important was to eliminate the undefined torque contributions of the interface inside of the ring by adopting a 2-D double wall configuration². This is accomplished by replacing the bottom cup with a circular channel containing the fluid.

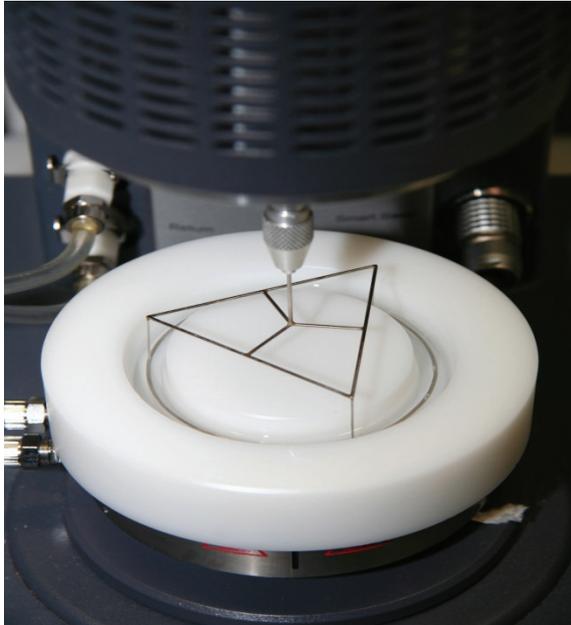


Figure 2. DWR setup on the AR-G2 rheometer from TA Instruments.

The ring is made of Pt/Ir and the circular channel of Delrin[®], a material similar to Teflon. A stepwise edge in the vertical walls of the channel, machined at the height of the sub-phase fluid level, allows pinning of the interface – thus reducing the meniscus effect of the fluid at the outer and inner wall. The trough with the circular channel is positioned onto the standard Peltier plate of the rheometer. The ratio of outer and inner radius of the DWR is $\delta=1.11$. Under these conditions a more or less uniform shear rate between ring and wall can be assumed.

Table 1. Physical dimensions of the DWR geometry.

R_1 (mm)	R_2 (mm)	R_3 (mm)	R_4 (mm)
31,00	34,50	35,50	39,50

The ISO standard for coaxial cylinder system (bulk rheology) recommends a ratio $\delta=R_o/R_i$ of 1.0847. Therefore the equations for the stress and strain constants are adopted from the double wall cylinder geometry simply by removing the cylinder length.

$$K_\gamma = \frac{1}{\left(\frac{R_2}{R_1}\right)^2 - 1} + \frac{1}{1 - \left(\frac{R_3}{R_4}\right)^2} \quad (1)$$

$$K_\tau = \frac{1}{2\pi(R_2^2 + R_3^2)}$$

The dimensions of the DWR geometry, given in Table 1 are chosen such that the average shear rates of the inner and outer shear sections are the same. In order to obtain the desired rigidity, the ring is attached with three legs to the support structure (Fig. 2).

The flow and deformation of an interface will entail deformation and flow in

the surrounding bulk phases. The intimate coupling between the flow in bulk and at the interface is often complex to analyze. Typically, if the coupling is ignored one will tend to overestimate the surface rheological properties. Due to the small contact area of the geometry and the sub-phase, the torque contributions of the sub-phase are considerably reduced and a correction⁷ is only necessary for sensitive and fragile interfaces.

EXPERIMENTAL

The performance of the DWR will be demonstrated by measuring the interfacial shear properties of SPAN65[®] (Sorbitan tristearate) at the water-air and water-oil interface. SPAN is a much larger molecule and provides strong films with pronounced viscoelastic behavior at the water-oil interface. A 0.5M solution of SPAN in the hydrophobic phase has been used and the interfacial shear properties at the water-dodecane interface were measured. A 1mM solution in chloroform was used to spread the SPAN molecules at the water-air interface.

The water was obtained from a pure water system (Milli-Q Integral 3). The trough with the circular channel and the ring were carefully rinsed with purified water before each experiment. The ring was cleaned in a flame to remove all organic residues. The temperature was held at 20°C during all experiments.

RESULTS

A series of experiments was performed with the surfactant SPAN65[®]. The strain sweep performed on a film of SPAN at the water/dodecane interface exhibits a response, seen for many bulk materials (Fig. 3).

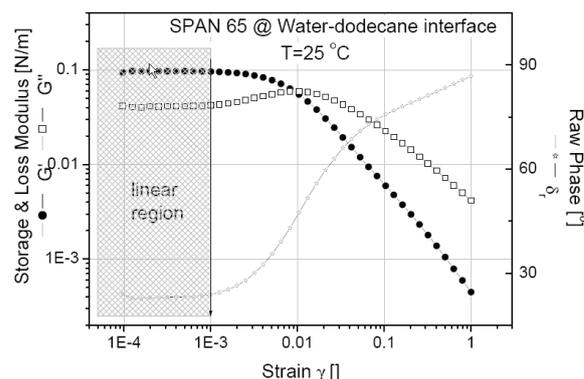


Figure 3. Strain sweep experiment for a SPAN film at the interface between water and dodecane ($c=0.5\text{mM}$, $T=20^\circ\text{C}$).

The onset of the non-linear behavior is around 0.1% strain amplitude and the interfacial loss modulus goes through a maximum before decreasing along with G_s' in the nonlinear region. The frequency sweep, performed in the linear region at 0.1% strain amplitude shows a typical viscoelastic response with a crossover point at 0.2 rad/s (Fig.4). Above 30 rad/s, the raw phase increases to 180° – system inertia dominates the experiment beyond this frequency.

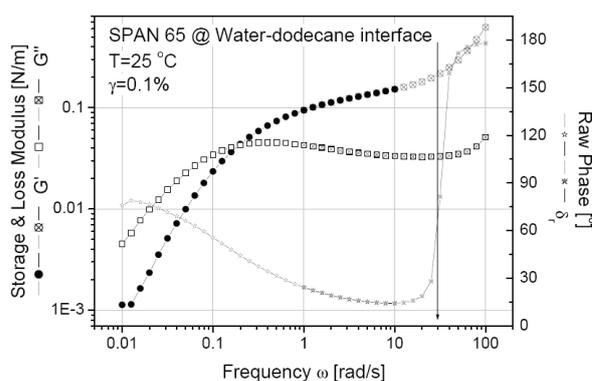


Figure 4. Frequency sweep experiment for a SPAN film at the interface between water and dodecane ($c=0.5\text{mM}$, $T=20^\circ\text{C}$).

In addition to the tests at the water-oil interface, experiments were performed at the water-air interface. In order to run these tests, the surfactant SPAN was spread onto

the water from a 1mM solution in chloroform. After the evaporation of the solvent, the test was started. Different surface loadings of surfactant from 0 (no surfactant) to 4.3 molecules per nm² were analyzed.

Figure 5 shows the interfacial storage and loss modulus as a function of the applied strain at a frequency of 1 rad/s. With increasing surface loading, G_s' and G_s'' increase and the plateau modulus at a surface loading of 4.3 molecules/nm² is 0.03 N/m. Note that for all test runs the raw phase was significantly below 180° and system inertia contributions could be corrected.

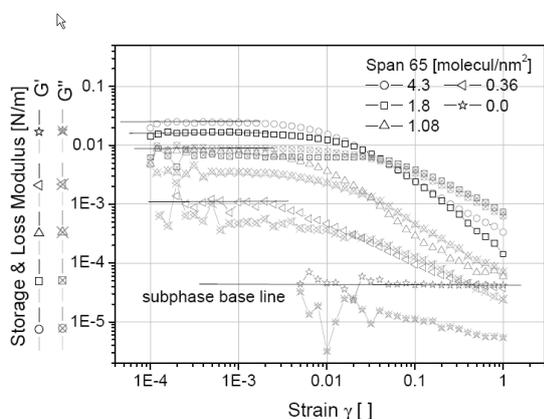


Figure 5. Strain sweep experiments for a SPAN film at the interface water-air at various surface loadings (T=20°C).

CONCLUSION

A new geometry for surface rheological measurements for both water-air and oil-water interfaces that can be attached to a commercial rheometer has been presented. The setup consists of a double wall ring and incorporates the advantages of both, the Du Noüy ring and the bi-cone. Due to the reduced contact area between the bulk phase and the geometry, the intrinsic sensitivity of the device is increased and the relative magnitudes of the sub-phase torque contributions are significantly reduced relative to the surface contributions. Any sub-phase corrections are only necessary for

very fragile interfaces with interfacial viscosities below 10⁻⁵ Pa.s.m.

Test results in oscillatory shear have been presented SPAN. An important consideration when using the new attachment on CMT (stress controlled rheometers) with no separate torque measurement is the system inertia, which can mask the real material behaviour at frequencies above 1 rad/s, depending on the experimental setup.

REFERENCES

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