

Double Wall Ring Geometry to Measure Interfacial Rheological Properties

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ABSTRACT

The rheological characterization of thin liquid layers at interfaces is motivated by their intensive use in a variety of industries, ranging from enhanced oil recovery, food technology to biomedical applications. The most used devices for measuring interfacial properties that can be attached to a commercial rheometer are the Du Noüy ring, disc and bi-cone geometry. The Du Noüy ring is only suitable for purely viscous interfaces. The bi-cone and disc geometries can be used for viscous and viscoelastic interfaces, but the sensitivity is limited because these device intrinsically posses a large area in contact with the bulk fluids. A new double-wall ring geometry to be used with a standard rotational rheometer has been developed. It has the advantages of a good intrinsic sensitivity due to a small area in contact with the bulk phase and well defined flow fields that enable bulk and surface contributions to be separated. The double-wall ring geometry has a square edged cross-section and is used with a temperature controlled bottom circular channel arrangement to contain the fluid. Results on model interfaces show that the new geometry is able to measure viscous as well as visco-elastic interfaces in both continuous and oscillatory shear 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 effect of particles, surfactants or proteins at these interfaces in a variety of industries such as food, biomedical, enhanced oil recovery and so forth. Interfacial shear rheometry measures the mechanical strength or the shear viscosity of an interfacial layer i.e. the adsorbed monomolecular film at a liquidliquid or liquid-gas interface. Typical interfacial viscosities for insoluble monomolecular films range from 10⁻⁵ to 10⁻² Pa.s.m. A number of methods have been developed to investigate the surface and interfacial shear properties [1]. Often, custom made devices have been built to measure the properties of the interface, for example, the canal surface and deep channel surface viscometers [2], disk and bi-cone rheo-meters [3] and the magnetic rod rheometer [4].

Recently several devices to study the interfacial rheological properties to be used in conjunction with rotational rheometers have been suggested. The most common ones are the bi-cone/disc [5] 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 with the perimeter in contact with the interface. The Du Noüy ring, originally developed for surface tension measurements does not fulfill all the requirements for shear measurements. Despite the sensitivity due to the re-



Figure 1: Schematic representation of the DWR configuration

duced geometry surface exposed to the sub phase, does the Du Noüy ring have a number of issues. For example the small gap assumption is not fulfilled and the contribution of the surface inside of the ring is not taken into account. The round cross-section of the ring is not ideal for pinning the interface, the interface can easily slip over the ring, avoiding coupling.

THE DOUBLE WALL RING (DWR)



| R1 | R2 | R3 | R4 | а | b |
|-------|-------|-------|-------|------|------|
| тт | тт | тт | тт | тт | тт |
| 31.00 | 34.00 | 35.50 | 39.50 | 1.00 | 0.70 |

Table 1: Physical dimensions of the DWR geometry.

The double wall ring (DWR) geometry shown in figure 1 is a result of combining the best features of both, the Du Noüy ring and the bi-cone. The round shape has been replaced with a square edged 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. The undefined torque contributions of the interface inside of the ring have been eliminated by adopting a 2D double wall configuration [6]. This is accomplished by replacing the bottom cup with a circular channel containing the fluid. The ring is made of Pt/Ir and the circular channel of Delrin®, a material similar to Teflon. A step 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 wall.



Figure 2: DWR setup on the rheometers from TA Instruments. a) DHR b) ARES-G2



Figure 3: Layout of the DWR geometry and boundary conditions for the sub-phase velocities

The new DWR geometry can be mounted onto CMT (combined motor transducer) as well as on SMT (separate motor transducer) rheometers from TA Instruments (Fig. 2). On the CMT rheometer, the ring is rotating/ oscillating, on the SMT the outer cup is rotating/oscillating whereas the ring is attached to a separate torque transducer. The trough with the circular channel is attached to the Peltier plate for the DHR (Fig. 2a)) and to the APS for the ARES-G2 (Fig. 2b)). Furthermore do all features and capabilities of CMT and SMT rheometers apply to the 2D rheometry.

The ratio of outer and inner radius of the DWR is δ =1.11. Under these conditions a more or less uniform shear rate can be assumed. The ISO standard for concentric cylinder system (bulk rheology) state a ratio δ =R_a/R_i of 1.0847. The equations for the stress and strain constants are adopted from the double wall cylinder geometry.

The dimensions of the DWR geometry, given in Table 1 are chosen such that the

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

average shear rate of the inner and outer shear sections are the same.

SUB-PHASE CORRECTION

Results from interfacial shear measurements are always overestimated due to the fact that the interfacial film drags the subphase along. The relative contributions of the surface stress and the stress arising from the bulk are expressed by the Boussinesq number:

$B_o = \eta_s / (\eta L)$

 η_s is the surface viscosity, η the bulk viscosity and *L* is a length scale associated with the measurement technique. For the DWR, *L* is 0.7mm, which corresponds to the side length of the square ring.

Because of the very small contact area geometry/sub-phase of the DWR, the measured torque contributions of the sub-phase are considerably reduced, such that corrections for sub-phase are only necessary for sensitive and fragile interfaces [7]. The sub-phase drag correction is based on a finite difference calculation. The velocity profiles in the sub-phase can be determined using the Navier Stokes equation. In cylindrical coordinates (R, θ , z) they can expressed as follows [7]:

 $v_{sp}(r,z)$ is the unknown sub-phase velocity

$$\eta_{sp}\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{sp}\left(r,z\right)\right)\right) + \frac{\partial^{2}v_{sp}\left(r,z\right)}{\partial z^{2}}\right]$$
$$= \rho \frac{\partial v_{sp}\left(r,z\right)}{\partial t}$$

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in θ direction. For a continuous shear experiment, the velocity is the product of the parameter a_{sp} and the angular velocity, for the oscillation shear experiment a_{sp} is multiplied with a sinusoidal oscillating velocity.

$$v_{sp}(r, z) = a_{sp}(r, z)\Omega$$
$$v_{sp}(r, z) = a_{sp}(r, z)\theta_o i\omega_o e^{-i\omega_o t}$$

The boundary conditions for the subphase velocities for the DWR setup at the ring and at the wall/bottom of the circular channel are shown in figure 3.

In order to solve the equations for the unknown velocity, the momentum balance at the interface needs to be established. This momentum balance takes into account a linear model for the surface stress tensor according to Boussinesq [8]. The stress condition at the interface reduces to [3]:

$$\frac{\partial v_{sp}(r,z)}{\partial z} = \frac{\eta_s}{\eta_b} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r v_s(r,z) \right) \right)$$

In the calculations only the interfacial shear viscosity v_s (not the dilatational) is taken into account. The interfacial viscosity is a complex number $\eta_i = \eta' - i\eta''$ in oscillation experiments. The determination of the corrected interfacial viscosity is based on an iterative approach. With the measured interfacial viscosity as starting value, the velocity field at the interface is calculated using the finite difference approach. Based on the velocity profile, the theoretical rheometer torque, consisting of bulk and surface contributions is evaluated. The theoretical torque value is compared with the measured torque value and a new interfacial viscosity is estimated according to:

$$\eta_{k+1}^{(\sigma)} = \eta_k^{(\sigma)} \cdot \frac{M_{measured}}{M_{calculated,k}}$$

The iteration process continues until the measured and the theoretical torque converge. The algorithm stops after a certain number of iterations or after a tolerance val-



Figure 4: Experimental verification of the DWR sensitivity using ultrathin oil films. Raw and sub-phase

ue has been obtained.

EXPERIMENTAL

Performance check

In order to check the sensitivity of the DWR, the viscosities of ultrathin oil films, spread on the water surface are measured [7]. The oil is spread onto purified water by gently depositing a drop of high viscosity oil. The bulk viscosity of the oil used is 10 Pa.s. The theoretical interfacial viscosity for the films is obtained by multiplying the bulk viscosity with the film thickness. Tests on film thicknesses of 9, 5.4 and 0.39 micron have been performed. The experimental results were measured over a range of shear rates from 0.1 to 10 1/s. In figure 4 the dashed lines represent the theoretical values, the symbols the raw and corrected data points. The lowest interfacial viscosity that could be measured was of the order of $4x10^{-6}$ Pa.s.m (Bo=2.8), which corresponds



Figure 5: Strain sweep for a TTAB/NaSal film at the interface between water and n-decane (c=0.0024M, $T=20^{\circ}C$)

to a torque of approx. 60nN.m at 1 1/s.

Materials and Test procedures

The performance of the DWR will be demonstrated measuring the interfacial shear properties of 2 series of surfactant molecules TTAB (tetradecyltri-methylammonium bromide), CTAB (Cetyltrimetyl -ammonimum bromide) and SPAN65[®] (Sorbitan tristearate) at the water-air and water-decane interface.

TTAB and CTAB are relatively short molecules and are soluble in water. A 0.01M CTAB and 0.0024M TTAB/NaSal aqueous solutions were used in this investigation.

SPAN is a much larger molecule and provides strong films with pronounced viscoelastic behavior at the water-oil interface. A 0.5mM solution of Span65 in dodecane was used to build the interfdace at the waterdodecane interface. A 1mM Span 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 heated up red hot with a torch to remove all organic residues.

To load the sample the following general procedure was followed:

- 1. First the dense phase, water with or without the active ingredient is filled into the bottom channel up to the mark i.e. step in the wall.
- 2. If the ingredient has not been added to the water phase, it can be spread on the surface (with a solvent) for water-gas interfaces
- 3. Next the DWR was set at the interface
- 4. Last the oil phase was added for testing at water-oil interfaces (with the ingredient if not already added

to the water phase)

The Delrin® through is mounted on the Peltier environmental system of the rheometer. The temperature was held at 20°C during all experiments.

RESULTS

TTAB and CTAB

The 0.0024M TTAB/NaSal solution was filled into the trough, the ring set at the interface and n-decane gently deposited on top of the water phase. All experiments on TTAB were performed on the AR-G2.

The first experiment performed in the series is a strain sweep at 1 rad/s to detect the sensitivity limit and the extend of the linear viscoelastic range (Fig.5).

TTAB builds an elastic interface with a storage modulus ~ 40 times higher than the loss modulus at a frequency of 1 rad/s. The



Figure 6: Frequency sweep for a TTAB/NaSal film at the interface between water and n-decane (c=0.0024M, T=20°C) a) G's and torque b) G'. G" and raw phase

interfacial modulus G' has a value of $2x10^{-4}$ N/m and could be accurately measured down to 0.005 strain units. The corresponding torque value at this strain is on the order of 3 nN.m. The onset of non linear viscoelastic behavior is found at 10% strain.



Figure 7: Polar representation of the torque vector for the frequency data in Figure 6.

The next experiment consists of 5 consecutive frequency sweeps between 1 and 10% strain, performed on the same sample. The first run (Fig.6) is completely dominated by inertia, the torque changes with frequency squared ($\sim \omega^2$). At low frequency the modulus is approaching zero. The second run gave the same response in the inertia dominated region, however at frequencies below 1 rad/s a plateau value at 10^{-4} is obtained. For the 3^{rd} to the 5^{th} run, a plateau established at a level of 4×10^{-4} N/m. As time progresses the interface builds up slowly to reach a equilibrium after the 3rd run. Note, that the torque amplitude (magnitude) drops significantly at a frequency of ~ 1rad/s. The drop of the torque correlates with a step change of the raw phase from 0° at low frequency to 180° at high frequency (Fig. 6b)). At a raw phase of 180°, the results are dominated by the system inertia, only below a frequency of ~ 1rad/s do the measured results describe the material response at the interface.

With increasing strength of the interface, the inertia dominated region moves to higher frequencies. For the actual setup the maximum test frequency is between 1 and 2 rad/s.



Figure 8: Strain and frequency sweep for the CTAB film at the interface between water and n-decane $(c=0.01M, T=20^{\circ}C)$

The torque minimum at the onset of the inertia dominated region can easily be explained when representing the torque (stress) magnitude as a function of the raw phase in a polar plot (Fig.7). Since the interface is predominately elastic at all frequencies, the transition from the system inertia dominated to the material elasticity dominated regime, shows a straight line in the polar representation. At a raw phase of 90°



Figure 9: Strain sweep for a film of SPAN65[®] at the interface between water and dodecane $(c=0.5mM, T=20^{\circ}C)$



Figure 10: Frequency sweep for a film of SPAN65[®] at the interface between water and dodecane

the magnitude of the torque vector is minimum i.e. very close to zero; inertia and elasticity contributions cancel out.

The same series of tests was performed on a 0.01M solution of CTAB, however without any addition of Sodium salicylate Na-Sal. The strain sweep is similar to the one for TTAB/NaSal. The ratio G"/G' is smaller whereas the interfacial storage modulus in the linear region is approximately the same (Fig.8). The storage modulus is independent of frequency, the interface builds instantaneously and no time effects could be measured. The modulus value for G' ($4x10^4$ Pa.m) was obtained on the same sample on five consecutive frequency sweeps performed with a strain from 0.1 to 10%.

SPAN65[®] at the water/air and water/ dodecane interface

The second series of experiments was performed with the surfactant, Span65[®]. Span65[®] is a larger and more complex molecule and is not a linear chain. Experiments at the water dodecane interface were performed with the ARES-G2.

The strain sweep performed on a film of SPAN $65^{\text{(B)}}$ at the water/dodecane interface exhibits a response, seen for many bulk materials (Fig.9). The onset of the non-linear behavior is around 0.1% strain and the interfacial loss modulus goes through a maximum before decreasing along with G' in the



Figure 11: Flow ramp (Up and down) after pre-shear and after 1 hour equilibrium. The green stars are stedy state values from stress growth experiments (Figure 12)

non linear region. This behavior is typical in bulk materials for gel-like materials. The maximum in G" is attributed to dissipative structure arrangements at the on-set of nonlinear behavior [9]. In addition to the fundamental response, the intensities of the odd harmonic contributions have been measured. The 3rd relative harmonic intensity emerges from the noise at the onset of nonlinear behavior. At large strain the harmonic intensities $I_{3/1}$, $I_{5/1}$, $I_{7/1}$ and $I_{9/1}$ reach a plateau value. This behavior is similar to the bulk response seen for viscoelastic materials. The frequency sweep, performed in the linear region at 0.1% strain shows a typical viscoelastic response with a cross over point at 0.2 rad/s (Fig.10).

Steady state flow experiments have been performed by ramping the shear rate loga-



Figure 12: Stress growth experiments in the range of shear rates from 0.0001 to 10 1/s for a film of SPAN65[®] at the interface between water and dodecane (c=0.5mM, T= $20^{\circ}C$)



Figure 13:Strain sweep for a film of SPAN65[®] at the interface wate/air at various surface loadings $(T=20^{\circ}C)$

rithmically from 10^{-4} to 10 1/s. After preshearing, the viscosity in the ramp up tests starts low (Figure 11), increases and then reaches the flow curve at 0.01 1/s. In the ramp down the viscosity increases and reaches a plateau value below 10^{-4} rad/s at approximately 0.5 Pa.s.m. Note that after one hour equilibrium time, the viscosity at the start-up of the ramp matches up with the flow curve already at 3 10^{-3} 1/s.

Stress growth experiments in the range of shear rates from 10^{-4} to 10 1/s have also been performed (Figure 12). The response time is rather short, steady state is reached already after 10s for the lowest rate. The steady state viscosity values from the stress growth experiments superpose very well onto the flow curve in figure 11 (green stars). The linear viscoelastic start-up curve

has been calculated from the frequency data and shown as dark grey filled circles in figure 12.

In addition to tests at the water/oil interface, experiments were conducted at the water/air interface using the DHR. In order to perform these tests, the surfactant SPAN65[®] 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 8 molecules per nm² were analyzed.

Figure 13 shows the interfacial storage and loss modulus as a function of the applied strain at a frequency of 1 rad/s. An experiment with purified water only, provided a storage modulus G' of 4 10^{-4} N/m. At these test conditions system inertia dominates the experiment (Raw phase 180°). With increasing surface loading, G' and G" increase and the plateau modulus at a surface loading of 4.3 molecules/ nm^2 is in the range of 0.03 N/m. Note that for all runs the raw phase was significantly below 180° and inertia contributions corrected for. A strain amplitude of 0.1% was applied to obtain the frequency dependence of the films with the various surface loadings. At high frequency, the increase of G' with ω^2 is due to system inertia (Fig.14). With decreasing film strength, the onset of the inertia dominated region decreases in frequency. The film



Figure 14: Frequency sweep for a film of SPAN65[®] at the interface water/air at various surface loadings $(T=20^{\circ}C)$



Figure 15: Plateau modulus as a function of surface loading plotted with data obtained form Rehage et al [5]



Figure 16: Continuous shear curves as a function of the shear rate for a film of SPAN65[®] at the interface

with the lowest surface loading of SPAN65[®] has a modulus in the proximity of 5×10^{-4} N/m. The measured torque in this region is below 10 nNm. With increasing surface loading G' and G" increase, the cross over point is shifting to lower frequency.

The results of the storage modulus in the plateau region are plotted versus the surface loading and compared with results obtained by Rehage et al.[15] (Fig. 13). Below a surface loading of 2.7 molecules/nm², a mono layer film can be assumed. At higher loading multilayer films are forming and the elastic modulus is much less sensitive to the loading in this region. Continuous shear experiments were also conducted on the SPAN65[®] films at various surface loadings. The layers show significant shear thinning as expected (Fig.16). Sub phase correction becomes important below an interfacial viscosity of 10⁻⁵ Pa.s.m.

CONCLUSIONS

A new attachment to commercial rheometers for measuring the interfacial shear properties at water-air and water-oil interfaces has been presented. The setup consists of a double wall ring and incorporates the advantages of both, Du Noüy ring and bicone. Due to the reduced contact area between the bulk phase and the geometry, the subphase torque contributions are significantly reduced. Subphase corrections are only necessary for very fragile interfaces with interfacial viscosities below $10e^{-5}$ Pa.s.m.

Test results in oscillatory shear have been presented for two surfactant materials, CTAB and SPAN. Whereas CTAB builds highly elastic interfaces at the water-ndecane interface, do interfacial films of SPAN give a typical viscoelastic response. 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 behavior at frequencies above 1 rad/s, depending on the experimental setup.

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