Application Note

Interfacial rheology: Principle, applications, and instrumentation

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nterfacial rheology technology provides information on the behavior and interaction of molecules at interfaces, which is important for the application and processing of many materials of the general type: foods, beverages, pharmaceuticals, coatings, household and personal products, etc. It is the basis of many research programs, i.e., the stability of foams and emulsions, membrane technology, the development of new materials to replace natural substances such as saliva, and the development of aqueous products to replace solvent-based materials. This paper describes the CIR-100 interfacial rheometer (Camtel, Royston, Herts, U.K.) (Figure 1) as it applies to this mode of analytics in studying the above materials.

Principle

Interfacial rheology is the study of the deformation and flow of thin films of material at a liquid/ gas or liquid/liquid interface, where interface indicates the boundary between two phases. A distinction may be made such that surface rheology describes the study of the liquid/gas interface and interfacial rheology specifically deals with the liquid/liquid interface. A chapter in Collyer's book is devoted to this subject.¹

There are two primary methods for measuring the interfacial rheological properties of adsorbed (soluble) and deposited (insoluble) layers of surface active materials at an interface: interfacial shear, which equates to 2-D rotational bulk shear techniques, and interfacial dilation, which equates to 2-D bulk elongational techniques. Interfacial shear rheology involves a change of shape of the interface as it is sheared, which gives a direct measure of the mechanical strength of the adsorbed layer. Under the small strains subjected by this technique, the molecules in the interface are in a dynamic equilibrium with the bulk, and the interfacial pressure and tension are constant. Interfacial dilational rheology is determined by measuring the change in interfacial tension due to a specific change in interfacial



area, i.e., changing interfacial pressure. This is a measure of the resistance to compression and expansion of the adsorbed layer.

Using the standard measuring system, a glass dish, and a Du Noüy ring, the CIR-100 interfacial rheometer measures interfacial properties in simple shear using an oscillating technique. The ring and dish configuration can be seen as a coaxial cylinder with zero length, which enables geometry factors to be calculated as a 2-D model of the coaxial cylinder. If the sample dish is replaced by a miniature Langmuir trough (CIR-LT), interfacial shear properties can be measured against different interfacial pressures. In standalone mode, the CIR-LT can be used as a conventional trough to produce surface pressure versus area per molecule ($\prod A$) plots, and from these data the interfacial dilational modulus or Gibbs elasticity can be computed. By oscillating the barriers, the phase angle, and amplitude ratio between the input wave and the resulting output dynamic interfacial pressure enables the in- and outof-phase moduli to be resolved.

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Applications

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Stability of foams and emulsions

Interfaces are very important in foam and emulsion systems. Because of the number of bubbles or droplets in the system, the interfacial area can be enormous. As a result, the structural properties of the interface affect the physical properties of the foam and emulsion systems.

The surfaces of emulsion droplets and foam bubbles can be stabilized by proteins or surfactants (as an adsorbed layer), preventing coalescence, and maintaining stability. Proteins form highly elastic 2-D networks by unfolding and reacting with their neighbors around the droplets or bubbles; this layer provides mechanical strength that physically prevents coalescence. Surfactants rely on rapid mobility, and they drag a layer of liquid with them into the gaps between droplets or bubbles. This liquid layer acts as a lubricant and prevents coalescencethe Gibbs/Marangoni mechanism. If the viscoelasticity of the protein layer is lowered, e.g., by the presence of surfactants or emulsifiers, then the stability is vastly reduced (*Figure 2*). The effect can be quite dramatic, and it is the mechanism by which antifoams work on mainly protein stabilized foams. For surfactant stabilized systems, if the temperature drops below the melting point of the emulsion, the mobility of surfactants is halted and a fragile interface is formed. In commercial emulsion and foam systems, it is common for both surfactants and proteins to be present. This results in a mixture of both types of molecules at the interface, and the mechanism by which each type works to stabilize either system is



Figure 2 Stability mechanisms of proteins and surfactants.



Figure 3 Effect of surfactants on protein stabilized film.



Figure 4 Interfacial elasticity.

disrupted. By measuring the interfacial elastic modulus of an emulsion or foam, which has a viscoelastic protein stabilizing mechanism, the mechanical strength of the system can be quantified. This quantification can then allow the determination of the degree of springiness of the restoring force of the system.

If a typical protein solution has surfactant added to it, the result on the interfacial elasticity can be seen in *Figure 3*, where, for a pure $1-\mu M \beta$ -lactoglobulin, the interfacial elasticity grows strongly and reaches a high value. However, with the addition of small volumes of Tween 20 and sodium dodecyl sulfate (SDS), the decrease in film strength is dramatic.

Figure 1 CIR-100 interfacial rheometer.

Leveling properties of paints

Two aqueous paints with very similar bulk rheological behavior and surface tension exhibited very different finishes in a spraying application. Paint A used a formulation containing surfactant A, and paint B contained surfactant B. Paint A produced foam and wetted the substrate sufficiently, but had poor leveling qualities. Paint B did not produce

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Figure 5 Growth of interfacial elasticity of the natural soap body wash.



Figure 6 Interfacial viscosity of the natural soap body wash.

foam, wetted the substrate very well, and had an acceptable leveling quality. Interfacial rheology was able to differentiate the paint containing surfactant A, which caused foaming and poor leveling from that with surfactant B, which did not foam and had good leveling.

A comparison of the base resin of paints A and B showed that, although paint B initially had the highest interfacial elasticity, after a short period of time the modulus decreased, following the trend of the base resin. Paint A showed a steadily increasing interfacial elasticity (*Figure 4*). This property seems to correlate with the formulation that produced the foam and gave poor leveling.

The good wetting of the substrate is related to surface tension, and with both paints having good wetting properties and similar surface tensions, the effect is not surprising. Bulk rheological properties were the same; thus this technique was not able to distinguish between the different behavior of the paints.

Interfacial flow and deformation properties of a body wash

Two samples of commercial body wash were submitted for testing: solution BW-1, a natural soap-based system, and solution BW-2, a commercial surfactant. Three further samples of potassium laurate (KL), a commercial surfactant (CS), and a mixture of KL and CS at 30:70 were provided. BW-1 is known to contain both lauric and myristic acid in its formulation. Visually, the customer observed that BW-1 formed a rigid film with excellent foam stability, whereas BW-2 formed a very mobile film with significantly less foam stability. The three surfactant solutions showed no rigidity. The customer was looking for a method to distinguish body wash products based on their formulation (bulk rheology and surface tension values were very similar for BW-1 and BW-2). Very small differences in interfacial rheological properties were exhibited among BW-2, KL, CS, and KL-CS. However, BW-1 and BW-2 exhibited significant differences in both the interfacial elasticity and viscosity.

Figures 5 and *6* show interfacial elasticity and viscosity, respectively, for all samples. Except for the body wash containing the natural soap BW-1, all other samples showed insignificant levels of interfacial elasticity and viscosity. The strength of the film and the increase in viscosity grew rapidly after about 10 min, and within half an hour, the increase was so great that the limits of the range were reached for the applied measuring conditions.

Instrumentation

Traditionally, rheometers have been utilized almost exclusively to measure the bulk properties of materials. When rheological studies were conducted to analyze interfacial rheological properties, it was with a series of different designs of laboratory-built instrumentation. In those few cases in which traditional rheometers have attempted to measure the interfacial rheological properties, biconical geometries have been utilized that have high inertia, so that only very strong films could be measured. The CIR-100 interfacial rheometer has been designed to directly measure the interfacial rheological properties of materials quantitatively using a highly sensitive detection system.

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The rheometer is an oscillating stress-controlled instrument that uses a virtually frictionless suspension mechanism. The standard measuring geometry is a Pt/Ir Du Noüy ring. The sample vessels are either a fireproof glass dish for simple shear measurements, or a Langmuir trough for changing surface pressure measurements. The unit incorporates a high-resolution displacement sensor to record strain amplitude.

The CIR-100 has been designed to operate either in a normalized resonance mode² or



Figure 7 Normalized resonance response.



Figure 8 Controlled-stress response.

controlled-stress mode (*Figures 7* and *8*). These modes of operation allow the instrument to measure properties in two different frequency regimes: the NR mode, which accommodates frequencies greater than 2 Hz, and the CS mode, which handles frequencies less than 2 Hz. As with all sophisticated rheometers, the CIR-100 yields from shear to recoverable energy component, $G_{s'}$, and a low energy component, $G_{s''}$, computed in real time based on a calculated geometric factor and the raw input and output data. From these, all other rheological (interfacial) properties can be calculated.

References

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- 2. Sheriff M, Warburton B. In: Hutton J, Pearson A, eds. London: 299–316. The theory of a universal oscillatory rheometer for the study of linear viscoelastic materials using the principle of normalized resonance, theoretical rheology.

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