Surface Rheology and Interface Stability

Sandia National Laboratories

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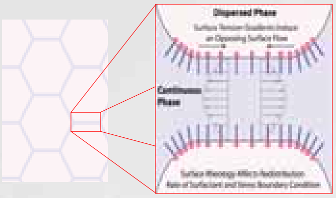
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Problem

- In shrinking to a microscale, there can be a *huge* increase in the influence of interfacial properties on microfluidic flows.
- Systems such as foams have large surface area relative to the bulk liquid volume, again leading to a large impact of interfacial rheology on flow and stability.
- The apparent viscosity of an interface can be much larger than that of the bulk liquid.
- Few laboratories have more than one advanced tool to probe the rheology of an air-liquid or liquid-liquid interface.
- Current understanding of the importance of interfacial rheology and current modeling capability for interfacial physics is limited.

Particles at an interface



Viscosity at an interface can be vastly different from the continuous phase

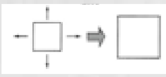
Approach

- We have brought together state-of-the-art interfacial characterization tools.
- We have developed new experimental techniques to directly probe the rheology at interfaces.
- We are continuing to use these new tools to:
  - Add to the state of knowledge about the influence of interfacial rheology
  - Collect data for model development and validation
  - Better understand foam stability

Surface Dilatational Rheometer (SDR)

- A surface dilatational rheometer was developed in-house.
- Interfaces can expand, so even so-called incompressible liquids can be influenced by a dilatational viscosity at an interface.
- Measure interfacial dilatational rheology by oscillating the volume of a pendant drop and measuring the changes in surface tension σ with surface area A.
- The surface dilatational modulus (E_s^*) is

$$A\frac{\partial\sigma}{\partial \ln A} \cong A\frac{\partial\sigma}{\partial A} = E_s^* = E' + iE''$$



Drop oscillating in volume has an interface that stretches

TA Instruments AR-G2 Du Noüy Ring Interfacial Rheometer

- TA instruments has developed several interfacial tools for use with their AR series rheometers: bicone geometry, du Noüy ring and double wall ring.
- Each of these geometries is placed at the interface and measures the shear interfacial rheology.
- To ensure the measured drag is dominated by surface viscosity, a large Boussinesq number, Bo, is also desired.

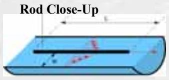
$$Bo_{DNR} = \frac{\text{Surface Drag}}{\text{Subphase Drag}} = \frac{\eta_s P}{\eta_b A} = \frac{\eta_s}{(0.36mm)\eta_b(\pi-\theta)}$$

η_s – surface viscosity
η_b – bulk viscosity
A – area of probe
P – perimeter of probe

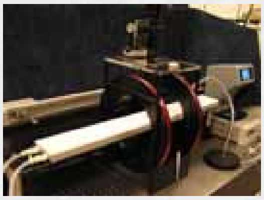
Sensitivity can be increased by decreasing the size of the probe.

KSV Interfacial Stress Rheometer (ISR)

- An interfacial stress rheometer (ISR) was used to measure the steady and dynamic surface rheology by applying an external magnetic field to actuate a magnetic needle suspended at the interface.



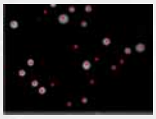
$$Bo_{ISR} = \frac{\eta_s P}{\eta_b A} = \frac{\eta_s}{(0.5mm)\eta_b(\pi-\theta)}$$

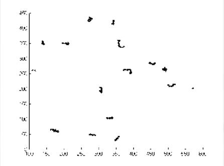


Microparticle Interfacial Rheometer (MIR)

- Microparticle Interfacial Rheology (MIR) analyzes the Brownian motion of microparticle probes suspended at the interface to investigate the effective viscosity.
- This technique is more sensitive but difficult to apply for highly elastic surfaces.

$$Bo_{MIR} = \frac{\eta_s P}{\eta_b A} = \frac{\eta_s}{(0.002mm)\eta_b}\left(\frac{\sin\theta}{1+\cos\theta}\right)$$

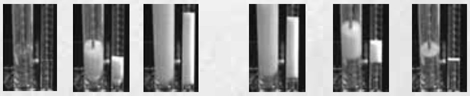




Results

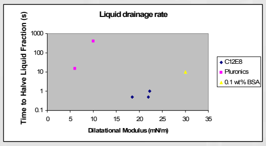
Foam Stability :

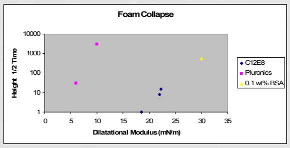
- To test the foamability and resulting stability, a foam is generated using a metal air stone with a 0.5 micron pore size. Foam stability including liquid drainage is tracked as a function of time.



Time=0 | 1.2 s | 6.6 s | $Time_{defoaming}$ = 7.2 s | 25.9 s | 44.9 s

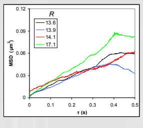
- Various instruments must be used to measure the range of surfactant systems we tested. For example,
  - Large proteins such as Bovine Serum Albumin measured with SDR, ISR, Du Noüy – too stiff for MIR
  - Polyoxamer copolymer and Ethylene Oxide ($C_{12}E_8$) measured with SDR, MIR – below the detection limit for ISR, Du Noüy
- Single measurement such as SDR predicts trends in foamability and stability only within a family of surfactants.



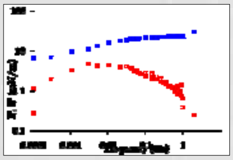


Sensitivity:

- MIR can measure shear viscosities on order of nPa-s-m
- Can examine dynamic response from 0.0001 to 1 Hz



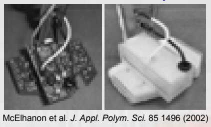
η_s = 18 nPa–s–m
= 0.000018 mN-s/m



Significance

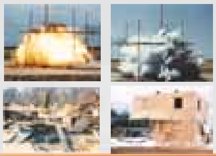
- Sandia now has an interfacial rheology lab including characterization tools with a wide range of sensitivity in surface forces from fN to nN.
- Better understanding of interfacial stability will allow better foams to be produced for a wide range of applications

Electronics — Foam Encapsulation



McElhanon et al. *J. Appl. Polym. Sci.* 85 1496 (2002)

Homeland Security — Explosion Suppression



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