

The rheology of two-dimensional systems

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Abstract

This paper discusses the rheology of complex interfaces comprised of amphiphilic materials that are susceptible to flow-induced orientation and deformation. The consequence of the coupling of the film microstructure to flow leads to nonlinear rheology and surface fluid dynamics. Experimental methods designed to determine the mechanical rheological material functions of fluid-fluid interfaces as well as local, molecular and morphological responses are presented. These include a newly developed interfacial stress rheometer, flow ultraviolet dichroism, and Brewster-angle microscopy. These techniques are applied to a number of complex interfaces ranging from low molecular weight amphiphiles to polymer monolayers. Nonlinear flow phenomena ranging from two-dimensional nematic responses to highly elastic surface flows that manifest surface normal stress differences and elongational viscosities are described.

1. Introduction

Fluid/fluid interfaces are ubiquitous in natural and technological processes. Amphiphiles can collect at these surfaces with the result that the interfaces can become rheologically complex. As a consequence, surface flows can display a variety of nonlinear phenomena that are reminiscent of their three dimensional counterparts. Examples where non-Newtonian interfacial rheology can be important include the deformation of droplets in blends and emulsions, the distortion and drainage of foams, thin film coating operations such as Langmuir-Blodgett deposition, the division of biological cells, and the transport of blood cells through fine capillaries.

Unlike bulk liquids, which are often taken to be incompressible, full rheological characterization of interfaces should consider dilatational deformations as well as flows that occur at constant surface density. It is possible to create surface flows that occur at constant surface area, however, and under these conditions one can properly measure rheological material functions such as the surface shear viscosity, dynamic shear moduli, and the interfacial shear compliance. In addition, many Langmuir films, where molecules are constrained to remain at the interface, are quite incompressible in certain regions of the phase diagram and dilatational effects can be neglected. The present paper is only concerned with rheological measurements at constant surface density. A reasonable starting point for a discussion of interfacial rheological measurements is the case of a Newtonian interface, which is characterized by the Boussinesq-Scriven constitutive equation:

$$\sigma_s = 2\eta_s \mathbf{D}_s + (\kappa_s - \eta_s)(\mathbf{I}_s \cdot \mathbf{D}_s)\mathbf{I}_s \quad (1)$$

where σ_s is the surface stress tensor (with units of force per unit length), \mathbf{D}_s is the surface rate of strain tensor, η_s is the surface shear viscosity (with units of force-time per unit length), κ_s is the surface dilatational viscosity, and \mathbf{I}_s is the surface identity tensor.

Interfacial rheology is relatively much less well developed when compared to bulk fluids and the recent book by Edwards, Brenner, and Wasan (1991) provides a detailed account of the development of conservation equations for these systems, as well as experimental methods and results. A variety of methods have been used in the past and these include the deep-channel viscometer, where the surface viscosity is measured indirectly by determining the surface velocity patterns traced by marker particles residing at the interface. This is an accurate method but is restricted to steady state flows. Other methods include the disk surface viscometer and the knife-edge surface viscometer.

In this paper an interfacial stress rheometer based on measuring the displacement of a slender, magnetic rod floating at the interface and subjected to a magnetic field gradient is described. This device is capable of a high degree of sensitivity and can accommodate time-dependent flows. The results of using this instrument to characterize polymeric and small molecule films are presented. It is demonstrated that a wide range of nonlinear, viscoelastic rheological phenomena is possible in two-dimensional systems. For example, Langmuir films can possess frequency dependent moduli, first normal stress differences, and shear thinning surface viscosities.

The origin of interfacial viscoelasticity is connected to the deformation and orientation of the microstructure of the

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films and for this purpose probes that can reveal flow-induced molecular or morphological rearrangements in thin films are useful. Two classes of techniques have been developed for this purpose: ultraviolet-visible dichroism to measure molecular orientation and flow-Brewster angle microscopy to image the morphology of complex interfaces. The combination of mechanical and microstructural measurements makes it possible to establish constitutive equations based on molecular models.

2. The langmuir trough and Langmuir isotherm

The experiments on molecularly thin films at fluid/fluid interfaces described in this paper utilized a Langmuir trough to establish the thermodynamic state (surface pressure, surface area, and temperature) of the system. Such a device is shown in Figure 1 and consists of a temperature controlled tray that is lined with Teflon. This is filled with the subphase until the top surface of the liquid coincides with the edge of the tray. Two horizontal barriers lined with Teflon are used to define the surface area of the film under study (defined as the area between the two barriers). These barriers are driven together or apart using a computer controlled motor. As the barriers are brought together, for example, this reduces the surface area available to a film and this will generally increase the surface pressure exerted by the film. The surface pressure is measured using a Wilhelmy balance. This device measures the force produced by a meniscus acting on a plate that protrudes through the interface.

A Langmuir film of amphiphilic molecules is established by floating a solution of the sample molecules dissolved in a volatile solvent. After the solvent has evaporated, a film of the molecules under study is left at the interface. As the film is compressed by bringing the barriers together, the surface pressure (defined as the difference between the surface tension of the interface in the absence of the film and its value with the film) will increase. Plotting the measured surface pressure against the surface area at a constant temperature produces the "pressure-area isotherm" and a schematic of such a plot is shown in Figure 2.

3. The interfacial stress rheometer

Measurement of the small forces associated with fluid/fluid interfaces requires a design that isolates the contribution of the interface from forces arising from the subphase (and the superphase for the case of a film contained between two liquids). The ratio of these two contributions is captured by the Boussinesq number, Bo , which is defined as

$$Bo = \frac{\eta_s}{\eta R} \quad (2)$$

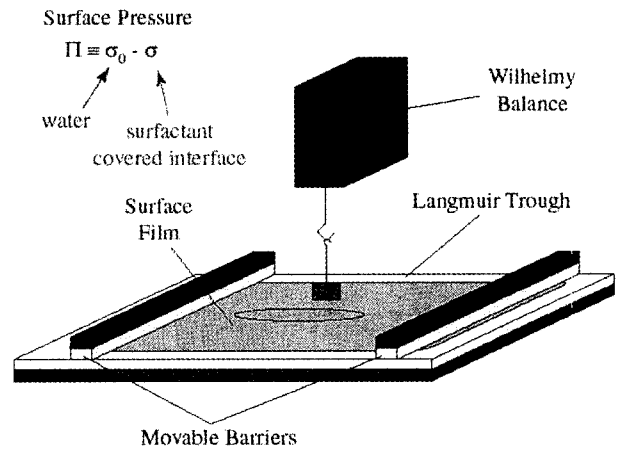


Figure 1. The Langmuir trough.

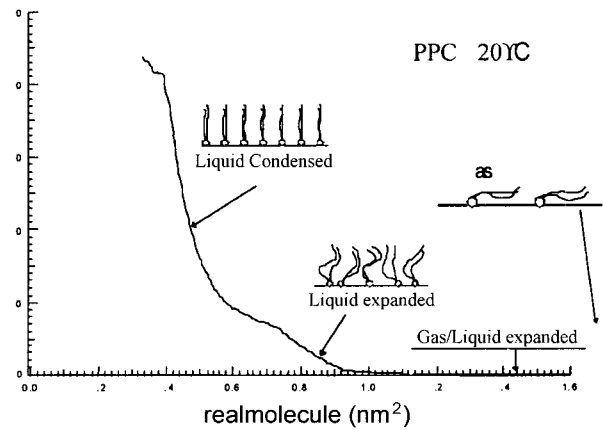


Figure 2. Langmuir isotherm for DPPC at 20°C.

where η is the subphase viscosity and R is a length scale associated with the physical device creating the flow field. In the limit of large Boussinesq numbers, the influence of the film will dominate the measured signal. Stone (1995) has analyzed the influence of the Boussinesq number on surface flows contained within a solid channel and compared his predictions against experiments performed by Swartz *et al.* (1994) using this flow geometry. This analysis assumed a Newtonian interface and demonstrated that the shape of a pressure driven flow between parallel boundaries will be parabolic when $Bo \gg 1$ and a "square root" profile when $Bo \ll 1$. When designing and operating an interfacial rheometer, it is essential that one recognize that the kinematics of the surface flow can be altered by variations in the Boussinesq number.

Figure 3 is a schematic diagram of the interfacial stress rheometer. A detailed description of the instrument is available in Brooks *et al.* (1999). At the center of the device is a flow cell consisting of a glass tube that has been cut in half and rests within a Langmuir trough. This figure depicts the arrangement that would be used to measure the rheology of an interface between a gas/liquid interface and the instrument can also be used to examine liquid/liquid

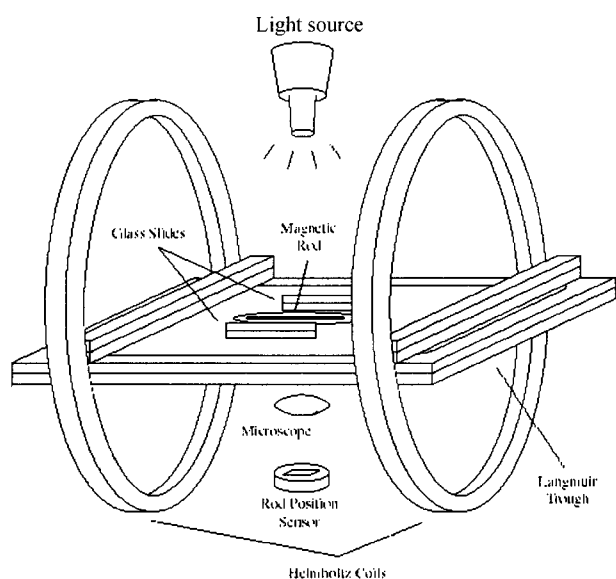


Figure 3. The interfacial stress rheometer.

systems. The subphase (typically water) fills the trough and the interface coincides with the top edge of the half-circular glass tube. Floating on the surface of the liquid is a thin magnetic rod. Normally a concave meniscus will form between the edges of the half-circular tube that will allow the rod to "self-center" within the tube.

The rod is set in motion by applying a magnetic field gradient throughout the space between two, large Helmholtz coils surrounding the Langmuir trough. As the rod glides parallel to its axis between the edges of the half-circular tube, a surface shear flow will be created and in the limit of large Boussinesq numbers (where the length scale in equation (2) is taken as the rod radius), a linear, simple shear flow will result at the surface. The measurement of the surface rheology is completed by determining the displacement of the tip of the moving rod as a function of time. This is accomplished by imaging the tip onto a position sensitive detector placed below a glass window at the bottom of the Langmuir trough.

The Helmholtz coils can be driven in a time dependent fashion to create sinusoidal forces acting on the rod, which would be used to determine the dynamic interfacial moduli of the interface. Alternatively, a steady force can be applied, which would result in a creep experiment. The latter experimental protocol results in the compliance and viscosity of the interface.

4. Optical measurements of flow-induced micro-structural rearrangements

4.1. Ultraviolet/Visible Dichroism

In general, the absorption of light by materials will be a strong function of wavelength. In an oriented system, it will also be sensitive to the relative alignment of the

direction of orientation in the sample and the polarization of the incident light. The latter phenomena are referred to as dichroism and can be used to measure the order parameter in flowing systems. In the case of ultrathin films, the challenge is to obtain sufficient signal when passing through a sample that in many cases is only one molecule in thickness. For this purpose, it is desirable to find a region of the spectrum where strong absorption occurs in the film but not in the subphase. For aqueous systems this makes the use of infrared wavelengths impossible. However, many amphiphiles show a strong absorption in the ultraviolet and some materials absorb quite strongly in the visible. Since water is transparent to these wavelengths, it is convenient to work in this spectral region.

The design of instruments to measure dichroism during flow processes is described in detail in Fuller (1995). To automate the measurement of dichroism and to make time-dependent measurements during flow, it is an advantage to introduce a modulation of the polarization of the incident light before it passes through the sample. In our case, the optical train consists of an Ar-ion laser that can generate discrete lines in the ultraviolet. This light is then polarized by passing it through a high quality Glan-Thompson polarizer and then through a photoelastic modulator (PEM). The PEM produces a sinusoidally varying birefringence within a transparent, amorphous crystal. The light then proceeds through the sample and strikes a detector. In this manner, the dichroism of the sample can be detected on time scales as fast as 1 ms.

In these experiments, the sample consists of an interface residing between two fluids and subjected to flow field. For this purpose the Langmuir trough is outfitted with a window of quartz so that UV-vis light can be transmitted through the film in the vicinity of the flow field. The flow fields are generated with a variety of flow devices with the majority of work being conducted using a four roll mill. This classical flow cell consists of four identical cylinders set on the corners of a square and set in motion in the manner indicated in Figure 4. This arrangement produces a two-dimensional extensional flow in the central region between the four rollers. This class of flow is characterized by straining of the fluid and interface elements in the absence of any rotation. When this flow cell is used, the light is transmitted through the center stagnation point where the molecules have the longest residence time in the flow. Figure 4 shows a sequence of two experiments where the flow is reversed. In this manner, the average orientation angle, χ , will switch from 0° to 90° . The UV dichroism experiment described above is capable of simultaneous measurements of the dichroism, $\Delta n''$ and the orientation angle, χ .

4.2. Brewster Angle Microscopy

When light is reflected from an interface at the Brewster

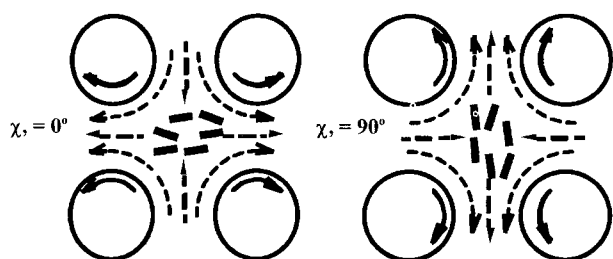


Figure 4. The four roll mill. In a flow reversal experiment, the average orientation angle, χ , will change from 0° to 90° .

angle, θ_B , light polarized in the plane of incidence will not be reflected. This physical event forms the basis for the construction of the Brewster angle microscope (Honing and Mobius, 1991) which is pictured below in Figure 5. With such an instrument, the presence of a thin film on the surface of a liquid will change the Brewster angle condition from what it is for the same liquid in the absence of a film. As a result, light impinging on the interface at the Brewster angle of the pure liquid subphase will be partially reflected when a film is present. If the film has a complex morphology, spatial variations in film thickness, composition, or orientation will cause the refractive index of the film to be a function of position. Imaging this reflected light onto a two-dimensional detector will produce a magnified view of the film and its morphology. In the presentation application, light is reflected off of interfaces subject to an imposed flow and BAM is shown to be an effective method of following the deformation and orientation of the film microstructure.

5. Flow visualization of non-newtonian interfacial flow

As will be presented in a later section, the non-Newtonian rheology of ultrathin films can lead to interfacial flows that are qualitatively different when compared against the response of Newtonian interfaces. These departures in macroscopic surface flow are most evident when the interfaces are forced to negotiate through

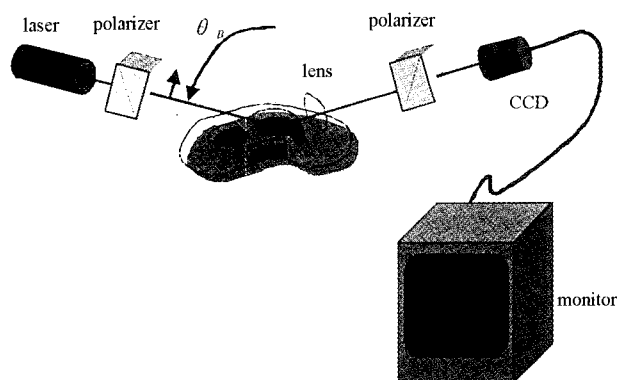


Figure 5. The Brewster angle microscope.

complex geometries where the flows are superpositions of simple shear and purely elongation deformations. For that reason, it is of interest to utilize benchmark complex flows that have proven to be important to reveal bulk non-Newtonian flow phenomena, with contraction flows being among the most important example. Similar strategies can be carried over to two-dimensional systems within the confines of a Langmuir trough. In these experiments, solid barrier walls are placed within a trough in a way that forms a contraction flow channel that is open at both ends (Olson and Fuller, 1999). This is shown in Figure 6. The height of the contraction flow channel is equal to the depth of the Langmuir trough and the system is filled in a manner that places the fluid/fluid interface at a level that also coincides with this height. Interfacial flows of Langmuir films are created by "skimming" the interface through the contraction by sliding a flat Delrin bar across the surface in the direction parallel to the flow channel. This is accomplished in a manner that maintains the average surface pressure within the Langmuir trough constant. However, there will be a pressure drop along the path of the pressure-driven flow within the channel.

The streamlines associated with the interfacial flow are visualized by tracking the motion of small sulfur particles deposited on the surface. These particle trajectories were recorded using a video camera and frame-by-frame analysis of particle positions was used to determine the streaklines.

6. Applications

Four problems in interfacial rheology are presented here to offer the reader an appreciation of the range of nonlinear phenomena connected with non-Newtonian interfacial rheology and fluid mechanics.

6.1. Nematic interfaces: The isotropic-to-nematic transition in two dimensions

When rodlike polymers are forced together, steric constraints can act on the chains to produce a spontaneous alignment to a nematic, liquid crystalline state. This

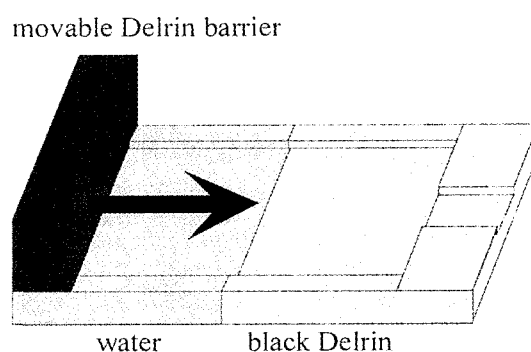


Figure 6. Contraction flow cell

phenomenon has received considerable attention for 3-dimensional, lyotropic systems and much of the resulting dynamics and rheology for bulk materials is well understood. In 2-dimensions, similar transitions are possible, but are predicted to be second order in contrast to the first order transitions found in 3-dimensions. Experimental evidence of liquid crystalline responses in thin films has only recently been reported (Maruyama *et al.*, 1998).

6.1.1. Materials

In this application, the rodlike polymer poly-p-phenylene sulfonic acid (PPPSH) has been used since it strongly absorbs ultraviolet light with a maximum absorption at 350 nm. The chemical structure of this molecule is shown below.

The polar SO_3H group anchors the chain to the water and the aliphatic tail, $\text{C}_{12}\text{H}_{25}$, remains above the air-water interface. In this manner, this rodlike chain is forced to lie flat on the interface.

PPPSH can produce stable, Langmuir monolayers but they are not very fluid. Instead, the resulting films are brittle and resist deformation. These systems can be fluidized, however, by creating a 2-dimensional solution upon the introduction of an appropriate low molecular weight amphiphile. In this work stearic acid (SA) is used to create a two-dimensional solution since it is known to have a Newtonian interfacial rheology under the conditions studied here. Since the stearic acid does not absorb light in the same location as the PPPSH, dichroism measurements will only respond to the orientation of the polymer.

6.1.2. Results

In the experiments to investigate nematic behavior in 2-dimensions, the four-roll mill was used to uncover the transition from isotropic to nematic interfacial flow response. This was accomplished by subjecting the sample to the flow-reversal protocol described in Figure 4. In this manner, the dynamics of the order parameter for an isotropic sample will be quantitatively different from those of a nematic. If one plots the product $\delta'' \cos 2\chi$ ($\delta'' = 2\pi\Delta n d/\lambda$ is the extinction and d is the thickness of the monolayer) against time, the dichroism will not change sign during the reversal of flow but $\cos 2\chi$ will change from +1 to -1. A nematic sample, however, will have a finite dichroism at rest whereas an isotropic sample will show a

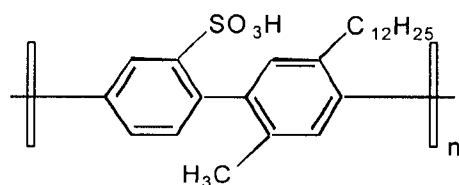


Figure 7. The chemical structure of PPPSH, a rodlike, amphiphilic polymer.

zero dichroism when it is fully relaxed in the absence of flow.

In Figure 8, $\delta'' \cos 2\chi$ is plotted against time for a 2-dimensional solution consisting of 40% PPPSH in stearic acid. Four separate experiments are shown here as the monolayer PPPSH/SA is compressed to increasing surface pressures. For the lower surface pressures of 3, 5 and 7 mN/m the interface behaves with an isotropic response. At time zero, the dichroism is zero and quickly increases to a steady state, negative value during the initial application of flow. Once the flow is reversed, however, the signal rapidly changes sign and reaches the same absolute magnitude in either direction. Once the flow is arrested, the orientation relaxes to zero but the relaxation time scale increases with surface pressure. At a surface pressure of 9 mN/m, however, the system behaves as a nematic. At rest, the sample shows a finite dichroism and is only partially relaxed upon the cessation of flow. Evidently, the system has undergone an isotropic-to-nematic transition at a surface pressure between 7 and 9 mN/m.

Evidence of the isotropic-to-nematic transition can also be observed in the mechanical rheology of this interface. Plotting the surface viscosity as a function of surface pressure produces the graph in Figure 9. In this graph, a clear kink in the slope of the viscosity as a function of surface pressure is observed at a surface pressure of 8 mN/m.

6.2. Influence of isomerization on interfacial structure and dynamics

The rheology of monolayers is strongly affected by the ability of molecules to pack on the interface and this is directly linked to molecular conformation. A convenient conformational transition for the purpose of study is the transformation between the cis to the trans configurations. This can be systematically accomplished using the amphiphile considered here: 4-Octyl-4-(3-carboxytrimethyleneoxy) azobenzene (8A3). With this molecule, illumination by ultraviolet light of wavelength 360 nm will take the material from the trans configuration to the cis configuration. Conversely, applying visible light above 450 nm will cause the reverse transformation to occur. Figure 9 shows the molecular architecture of 8A3 and the cis-trans conformation transformation.

Clearly, one would expect the trans state to allow for more efficient packing of the molecules on the surface compared with the cis conformation. In this study, Brewster angle microscopy was used to image the morphology of films produced in both isomeric states. Since this molecule strongly absorbs ultraviolet light in the range of 250 nm, dichroism at this wavelength can be used to measure the order parameter of 8A3 films subject to extensional flows using the four-roll mill. It is important to note that the wavelength of 250 nm used in the measurement of dichroism is substantially removed from the wavelength of

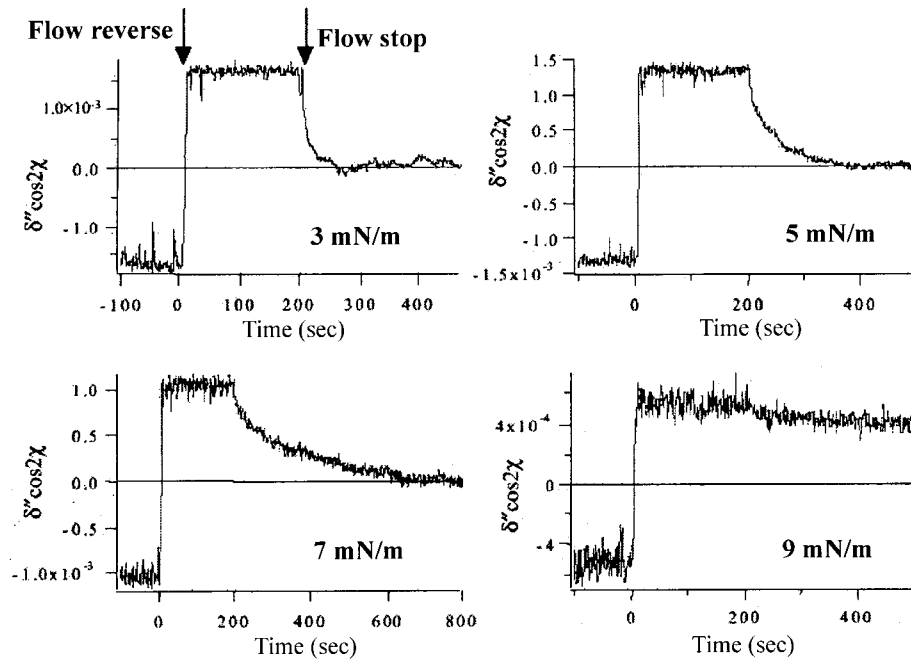


Figure 8. $\Delta n'' \cos 2\chi$ versus time for a 40/60 2-dimensional solution of PPPSH in SA for various surface pressures.

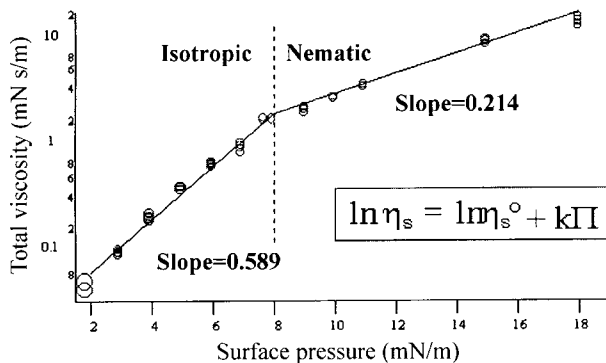


Figure 9. Surface viscosity of a 40/60 PPPSH/SA solution as a function of surface pressure.

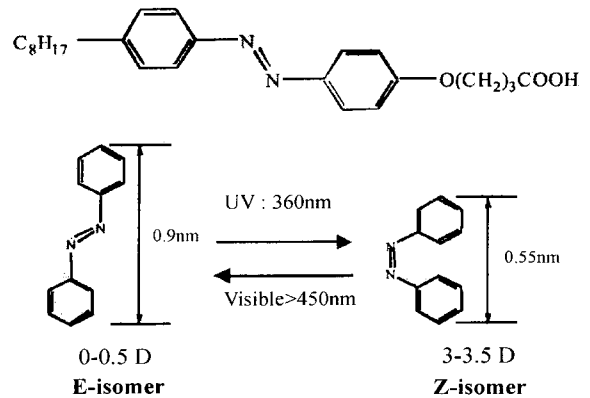


Figure 10. Molecular architecture of 8A3 and the cis-trans conformational transition.

360 nm used in the isomerization transition.

6.2.1. Equilibrium isotherms and structure

Figure 11 shows the pressure-area isotherms for a monolayer of 8A3 for both the trans and cis states. The cis conformation produces a much more compressible monolayer and the associated BAM image shown in this figure reveals an amorphous texture. On the other hand, the trans state isotherm contains a distinct "kink" at a surface pressure of approximately 13 mN/m that separates two phases labeled NN and NNN. BAM images of these two phases indicate a crystalline domain structure. It would appear that the trans conformational state leads to a more efficiently packed molecular structure and one would expect the rheological responses of the cis and trans states to be quite different.

6.2.2. Mechanical and optical rheometry of 8A3

Flow-induced dichroism measurements of 8A3 were conducted using a wavelength of 250 nm. As in the case of the PPPSH monolayers, a four-roll mill was used to induce two-dimensional extensional flows. The trans conformational states were found to produce very strong dichroism signals, indicating that flow-induced orientation of the 8A3 molecules was possible in this case. The cis conformation, however, was not orientable and showed no dichroism. In Figure 12, the dichroism of both phases of the trans state is plotted as functions of time following a flow-reversal sequence. The two phases show qualitatively different behaviors: the lower pressure NN phase (the solid curve in Figure 12) responds as an isotropic layer whereas the NNN phase (the dashed curve) has the sig-

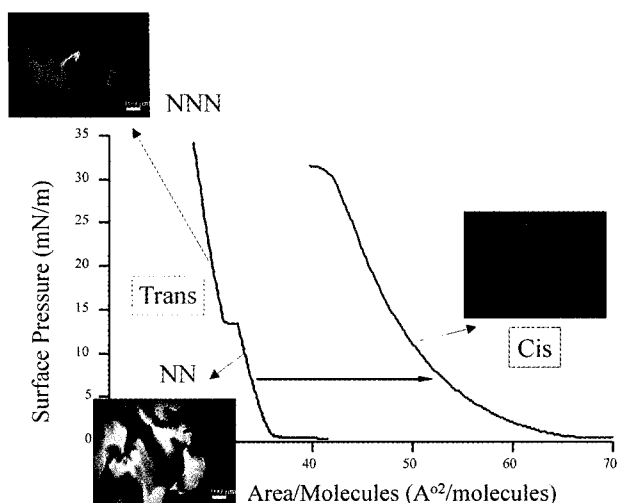


Figure 11. Isotherms and Brewster angle microscope images of 8A3 in the trans and cis states. Note that the trans state consists of two separate phases.

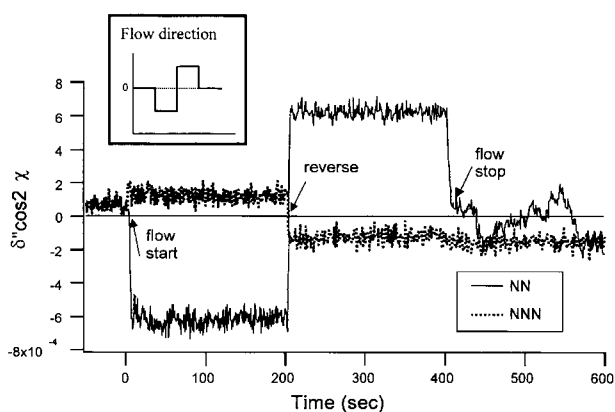


Figure 12. Isotherms and Brewster angle microscope images of 8A3 in the trans and cis states. Note that the trans state consists of two separate phases.

nature of a nematic. It is also interesting to note that the two signals in Figure 12 are of opposite sign, indicating that the same orientation of the principal axis of strain in the flow produces orthogonal orientations of the 8A3 molecules in these two phases.

Figure 13 shows the dynamic surface viscosities of the cis and trans states of 8A3 as functions of surface pressure. The cis state was found to have a surface viscosity that is relatively independent of pressure and several orders of magnitude lower than the trans state. Although not shown here, the cis state surface viscosity was found to be Newtonian and independent of the applied shear rate. The trans state viscosities, on the other hand, were observed to be shear thinning. The transition from the NN phase to the NNN phase was accompanied by a large, order of magnitude jump in the surface viscosity.

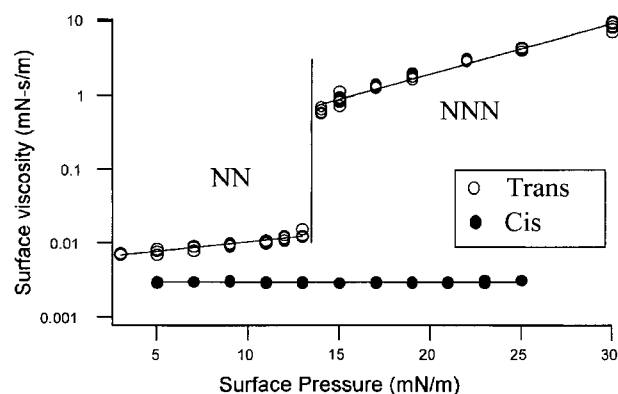


Figure 13. The dynamic surface viscosities of the cis and trans states of 8A3.

6.3. Non-Newtonian Surface Fluid Mechanics of Polymer Monolayers

In this final application, the consequences of non-Newtonian interfacial rheology on interfacial fluid mechanics was explored by examining the interfacial flow of an elastic, polymer monolayer through a complex geometry. The geometry chosen was the 4 to 1 contraction shown in Figure 6. The polymer used was a high molecular weight, flexible poly (octadecyl methacrylate) (PODMA) of molecular weight 331,000 and polydispersity index of 3.3. This amphiphilic polymer is known to lie flat on the air/water interface. The response of this polymeric interface was compared against the flow of arachidyl alcohol, a fatty alcohol that is known to have a Newtonian interfacial viscosity.

Figure 14 shows creep curves for both arachidyl alcohol and PODMA. The zero shear viscosities of both materials are quite close (0.028 and 0.034 mN-s/m, respectively). However, the PODMA monolayer is clearly non-Newtonian and the relaxation time of the film was measured to be 2.9 sec.

6.3.1. Results

Interfacial flows of arachidyl alcohol and PODMA monolayers through 4 to 1 contractions are shown in Figure 15. These reproductions of the surface streamlines were produced by tracking the trajectories of sulfur particles deposited on the surface. The Newtonian arachidyl alcohol monolayer produced a flow field with an absence of corner vortices at all values of the surface flow rates. The PODMA monolayer flow, however, possessed large vortices that are reminiscent of those found for bulk, elastic liquids (Ryssel and Brunn, 1999). This response is evidence that these molecularly thin layers are highly elastic and would be expected to have positive first normal stress differences and large surface extensional viscosities.

7. Conclusions and future outlook

This paper establishes the monolayers comprised of

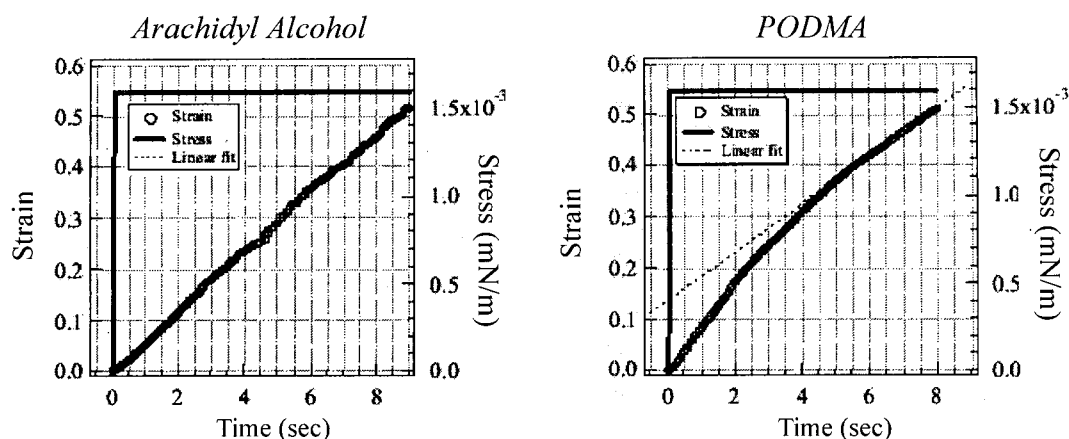


Figure 14. Constant stress creep response curves from arachidyl alcohol and PODMA. The surface pressure of the arachidyl alcohol was 30 mN/m and for the PODMA it was 5 mN/m.

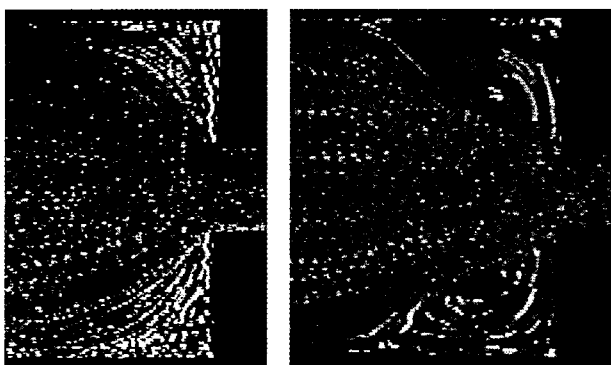


Figure 15. Contraction flows for arachidyl alcohol and PODMA at mean surface pressures of 30 and 5 mN/m, respectively. The flow is from left to right.

orientable or deformable amphiphiles can be characterized by non-Newtonian surface rheologies. These systems can be nematic in character if the constituent molecules are rigid and anisotropic in shape. Other systems, such as the PODMA shown in the last example, are amorphous, but subject to flow-induced deformation. As a result of flow-induced changes in film microstructure, these layers can display highly nonlinear flow phenomena. These rheological nonlinearities can be expected to play profound roles many problems of technological and biological interest. For example, the addition of surface-active species to emulsions and blends is known to stabilize these systems against coalescence. One explanation for this stabilization is the development of highly viscoelastic interfaces that hinder the drainage of matrix fluid between approaching droplets. Other examples, such as cell division where structured, bilayers are forced to strongly deform can also

be expected to strongly depend on interfacial rheology. There is a need for new analytical tools to examine these systems and this paper describes the application of both mechanical and optical methods to elucidate the behavior of ultrathin films. As data on surface rheological effects becomes more available, there will be a subsequent need for accurate constitutive models that properly account for the various microstructures that can be present at fluid-fluid interfaces. These problems connected to the flow of complex interfaces present important, new opportunities for experimentalists and theorists in rheology. On the side of theory and analysis, there is a need to develop appropriate constitutive models and to predict the nature of interfacial flows that account for coupling to the subphase.

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