

Description and Application of an Interfacial Viscometer

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Synopsis

This paper describes an interfacial viscometer. Rheological data of polymeric surfactants were obtained with the use of the instrument for liquid-liquid and liquid-gas interfaces. The surfactants studied were methylcellulose, poly(vinyl alcohol), polymer of diethylene glycol *n*-butyl ether acrylate, and sulfonated poly(vinyltoluene). Investigations were conducted over a wide range of temperatures and concentrations of the surfactants in the liquid phase. The instrument was used to obtain surface area coverage data for the surfactants studied. The experimental data were compared with theoretical calculations. The data indicated that the absorbed film at the interface was an irregular film, i.e., not an ordered packing of the molecules at the interface. Significance of interfacial viscosity on droplet break-up in a simple shear field was investigated. Droplet breakup studies substantiate the hypothesis that an absorbed polymeric film at an interface forms a complex viscous film.

INTRODUCTION

A pure liquid may exhibit a viscosity other than bulk viscosity at an air surface or at an interface with another pure liquid. However, many surface-active agents, commonly termed surfactants, absorb at an interface or surface of a solution. The films formed are usually quite viscous relative to the bulk solutions. A liquid-liquid or a liquid-air interface may have properties which are a counterpart of the bulk viscosity of the liquid, i.e., it may be resistant to shear stress. The surface or interfacial viscosity is defined as the ratio between shear stress and shear rate in the plane of the interface.

The study of interfaces has been revived in recent years. Investigators are becoming more aware of the importance of the properties of interfaces for studying such problems as stability of foams, liquid-liquid emulsions and suspensions, adhesion problems, coagulation, etc.

The purpose of this paper is fourfold: (1) To describe an interfacial viscometer. (2) To show how rheological properties of liquid-liquid or liquid-gas interfaces can be studied by such a rotational interfacial viscometer. (3) To show how interfaces possess complex rheological properties. It is important that investigators, especially people who are engaged in theoretical studies, be aware of the nature of interfaces. (4) To discuss applications of interfacial viscosity measurements. Examples are pre-

sented to illustrate how, by use of simple measurements with the interfacial viscometer, much insight can be obtained in solving many complex problems and correlating observations.

EXPERIMENTAL

Description of Apparatus

The apparatus used in these studies was a rotational torsion surface viscometer of the type described by Brown, Thuman, and McBain.¹ The schematic of the apparatus is shown in Figure 1, and a photograph of the actual equipment is shown in Figure 2.

The viscometer consisted of a knife-edged bob which hung freely from a torsion wire. Chucks held the torsion wire at each end by small brass cylinders to which the wire had been soldered. A removable cup containing the solution whose surface or interface was to be studied was placed on a turntable beneath the bob. A variable-speed motor drove the turntable through a 50:1 reducing gear. A frame supported both the bob and the turntable. The apparatus was mounted on a pedestal of concrete blocks with a $\frac{1}{2}$ -in. layer of foam rubber both above and below it. The motor was mounted on another such pedestal, and the driving shaft was of flexible (PVC) tubing. Thus, reasonably vibration-free operation was accomplished. A circular dampening trough, in which a viscous fluid such as mineral oil may be placed, was attached to the frame. An aluminum ring which fits in the trough was connected to the lower chuck above the bob. This arrangement prevented undesirable oscillation of the bob. Attached to the bob was a circular band with graduations in degrees inscribed on it, which were read through the telescope of a cathetometer. The frame, with bob and cup, was enclosed in an insulated wooden case made of $\frac{3}{8}$ -in. plywood with a Plexiglas window which could be opened for easy access to the apparatus. A small thermostat-controlled hairdryer in an upper compartment of the case circulated warm air about the apparatus when temperature effects were studied.

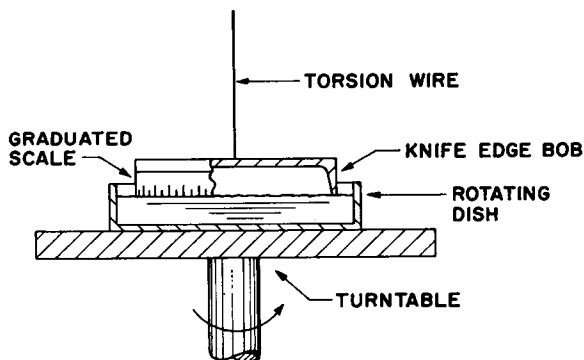


Fig. 1. Schematic of surface or interfacial rheometer.

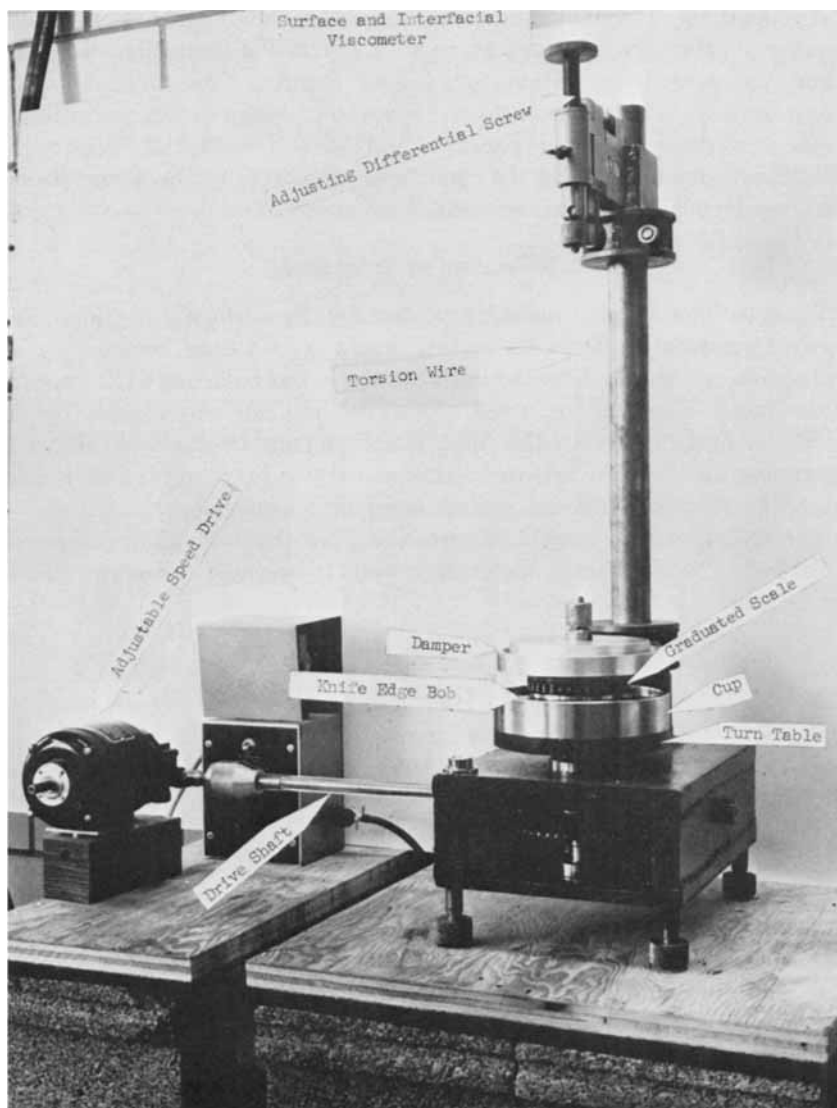


Fig. 2. Surface and interfacial viscometer.

It is important to note that the bob and cup should be constructed of nonmagnetic material; the first instrument built was not. The earth's magnetic field was strong enough to magnetize the parts, thus causing the bob to follow the cup when rotating. The magnetic effect overrode the torque due to viscous traction of the film. Furthermore, when the cup was stopped, the bob assumed an equilibrium position depending on the strength and direction of the magnetic field. The net result was that the zero reading shifted from day to day and could not be reproduced. The apparatus described in this paper was built from 4140 stainless steel.

Although the instrument described has been widely used by us and a number of other investigators, there are a number of limitations to its accuracy and sensitivity. Davis and Rideal² describe these limitations and how interfacial viscometers could be improved in design to correct for them. In the work described in this paper, the surface and interfacial viscosity are of sufficient magnitude that the corrections discussed by Davis and Rideal are a small contribution to the total effect observed.

Calibration of Apparatus

When the knife edge of the bob was placed on the surface of the liquid and the cup was rotated, a viscous surface would exert a drag, or shear stress, on the bob. The bob deflected until the stress was balanced by the torque of the wire. The drag, or stress, on the bob was not only exerted by the interfacial film, but also by the underlying liquid and by the liquid above it. Therefore, all the data had to be corrected by subtracting the deflection caused by the filmless liquid-gas or liquid-liquid interface.

The calculation of interfacial viscosity from the angular displacement of the bob corresponding to the angular velocity was made using the following equation³:

$$\eta_s = \frac{K(\theta - \theta_\omega)}{4\pi\omega} \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) \quad (1)$$

where η_s = coefficient of surface or interfacial viscosity; θ = angular deflection of the bob for a given angular velocity at the modified interface; θ_ω = corresponding deflection of the bob at the pure liquid-air or pure liquid-liquid interface; ω = angular velocity; R_b and R_c = radii of bob and cup, respectively; and K = wire torsion constant. In cgs units, η_s would have units of surface poise (dyne-seconds/centimeter).

The equation discussed in the previous paragraph was for an ideal Newtonian film. If the film had a yield (i.e., Bingham film), the equation had to be modified in the following manner:

$$\eta_s = \frac{K(\theta - \theta_\omega - \theta_0)}{4\pi\omega} \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) \quad (2)$$

where θ_0 is the extrapolated intercept of the linear portion of the deflection-versus-rotation curve on the line $\omega = 0$. The surface or interfacial yield was calculated from the following equation:

$$f_s = \frac{K}{4\pi} \theta_0 \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) \frac{1}{\ln \frac{R_b}{R_c}} \quad (3)$$

where f_s = surface or interfacial yield. In cgs units, f_s has dimensions of dynes/cm.

Strictly speaking, the equations for η_s apply only to Newtonian and ideal Bingham type surface or interfacial films. For non-Newtonian films, as

were nearly all the films studied, the equations given define a property called apparent surface or interfacial viscosity, which is a function of the shear rate. A graph of mean shear stress versus mean shear rate (rheogram) conveys more information and was more convenient, therefore, to present the data. The apparent viscosity was then found by calculating the ratio of the coordinates. The mean shear rate \bar{D} is given by

$$\bar{D} = \frac{2R_b R_c \omega}{R_c^2 - R_b^2}. \quad (4)$$

The mean shear stress $\bar{\tau}$ is given by

$$\bar{\tau} = \frac{K(\theta - \theta_\omega - \theta_0)}{2\pi R_b R_c}. \quad (5)$$

The torsional constant of the wire, K , was determined by measuring the period of oscillation T with an object of known moment of inertia I suspended by the wire:

$$\therefore K = \frac{4\pi^2 I}{T^2}. \quad (6)$$

Since the suspended mass included the chuck and dampening ring, the moment of inertia was not easily calculated. A more suitable method is to first measure the period T_0 of the chuck and dampening ring, then add a mass of material having a known moment of inertia, ΔI , and measure a new period of oscillation T_1 . K was determined by the following equation:

$$K = \frac{4\pi^2 \Delta I}{T_1^2 - T_0^2}. \quad (7)$$

Operating Procedure

A small amount of contaminant may have a major effect on the film properties; for this reason, it is necessary that the bob and cup be cleaned thoroughly before each usage. The following cleaning procedure was used:

First, the bob and cup were rinsed in distilled water, then in chloroform, and followed by distilled water again. They were then placed in warm (50°C–60°C) concentrated nitric acid for approximately 15 min and rinsed a final time in distilled water.

Two techniques were used for studying the rheology of interfacial films. One technique consisted of making solutions of known concentrations of the polymeric surfactants. A predetermined amount of the solution was placed in the cup. The viscometer bob was then adjusted so it was at the solution interface. This was accomplished by observing the meniscus at the edge of the bob. The second phase was then placed on top of the first solution. Measurements were then made by noting the angular deflection of the bob as a function of the rotational velocity of the cup.

The second technique consisted of first placing a pure solution in the cup. The bob was then placed at the surface by the technique previously de-

scribed. The second solution was placed on top of the first. With an accurate hypodermic needle, a known amount of solution of a fixed concentration of the polymeric surfactant was placed at the interface. If this is done with extreme care, it can be done accurately and reproducibly. Measurements were then made as discussed previously. It is important to note that in both techniques described, the angular deflection of the bob was corrected for the corresponding deflection at the pure liquid-gas or pure liquid-liquid interface.

The first method described will be referred to as the solution method for determining interfacial viscosity, and the second technique as the film method for determining interfacial viscosity. Intuitively, we felt that both methods should give comparable results. However, as will be shown later, this was not so.

Material Studied

Rheological properties of polymeric interfaces were obtained on the following materials: (1) sulfonated poly(vinyltoluene) (SPVT); (2) methylcellulose; (3) poly(vinyl alcohol) (PVA); (4) polymer of diethylene glycol *n*-butyl ether acrylate.

The surface viscosities were determined on a water substrate versus air, and interfacial viscosities were determined between ethylbenzene and water (unless otherwise indicated). All liquids and materials used in the experiments were of the highest purity available.

APPLICATIONS

Rheological Properties of Polymeric Interfaces

Rheograms of the four materials are discussed primarily to illustrate the complex behavior exhibited by polymeric surfactants.

Sulfonated Poly(vinyltoluene) (SPVT)

Figures 3 and 4 show SPVT films at the water-air and water-ethylbenzene interfaces. The rheological behavior of SPVT at each interface is similar; the viscosities are approximately of the same magnitude, probably being slightly higher at the water-ethylbenzene interface. The films show dilatant behavior. SPVT film, at low shear rates and at the water-ethylbenzene interface, exhibited pseudoplastic or Newtonian characteristics.

Methylcellulose

The methylcellulose used in these studies was Methocel MC Premium (100 cps). Figures 5 and 6 show the rheological behavior of Methocel at the water-air and water-ethylbenzene interface. Note that the two curves differ at the two interfaces.

Methylcellulose films are highly viscous and have a Bingham or plastic type of rheological behavior, i.e., they exhibit an apparent yield. Note the aging effect in Figure 6. The older film at the water-ethylbenzene interface

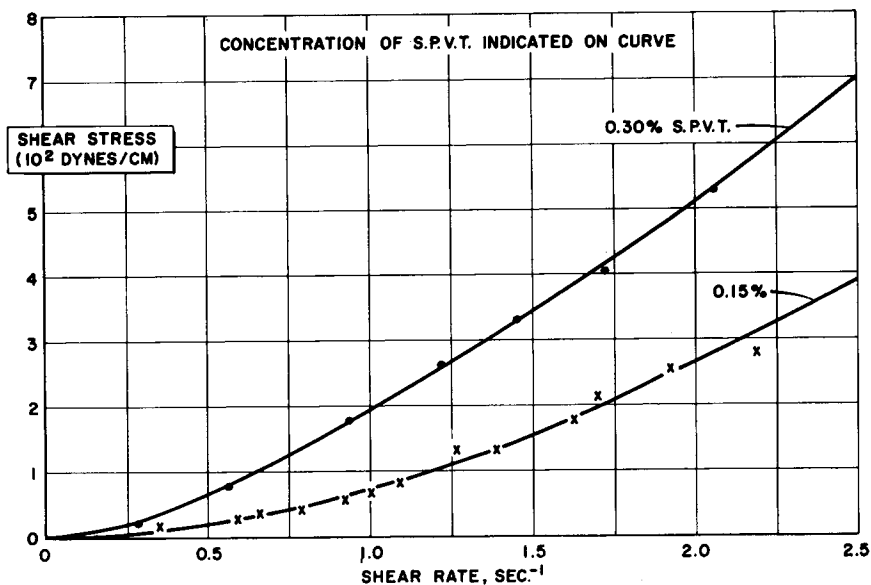


Fig. 3. Rheogram of SPVT at water-air interface.

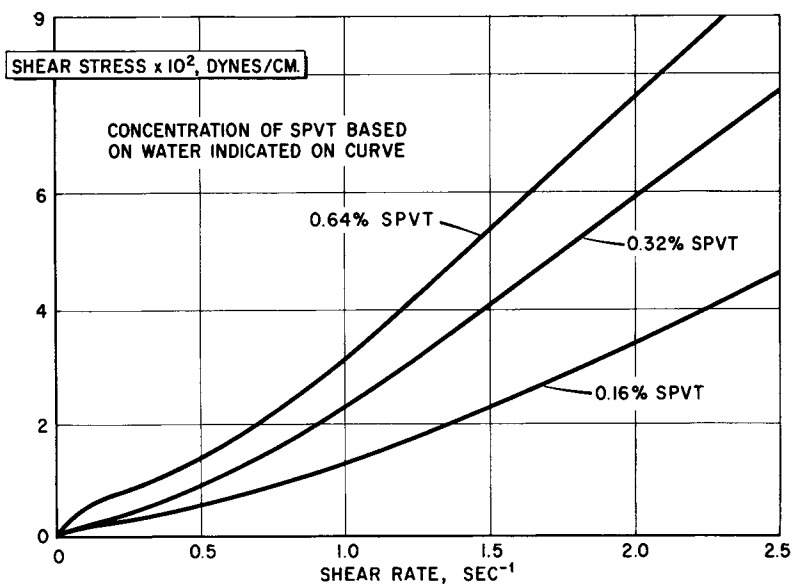


Fig. 4. Rheogram of SPVT at water-ethylbenzene interface.

produced a higher but irregular curve. The stress dropped sharply at three shear rates, indicating that the methylcellulose film becomes brittle with age.

All methylcellulose solutions do not form a film at the water-oil interface. A case in point is a concentration of 0.02% Methocel 60 HG in water at an

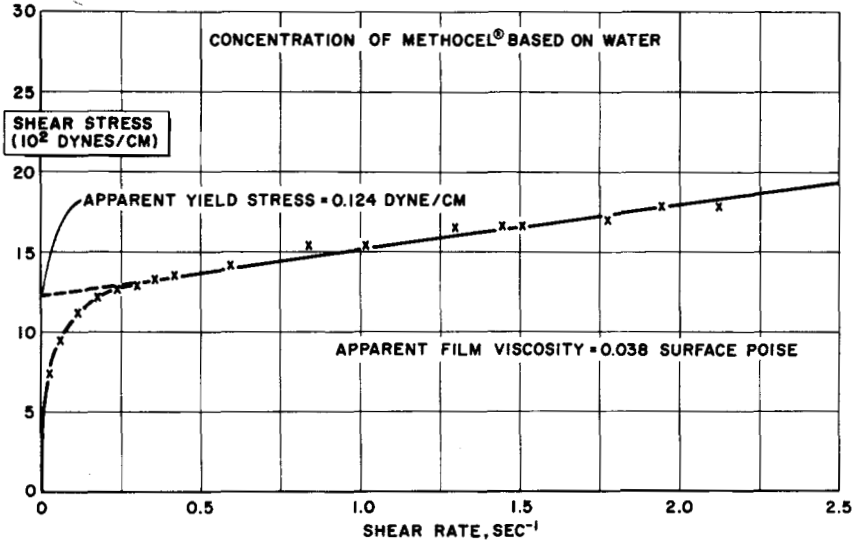


Fig. 5. Rheogram of 0.30% Methocel at the water-air interface.

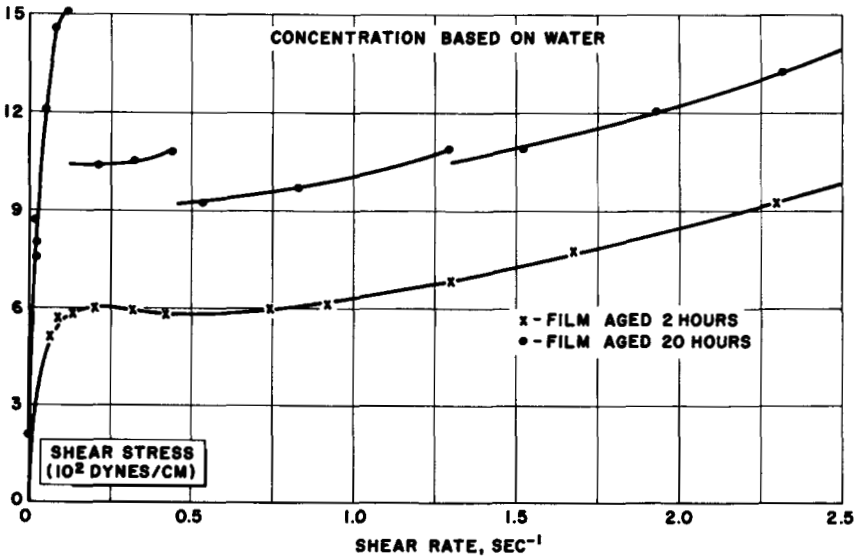


Fig. 6. Rheogram of 0.1% Methocel at water-ethylbenzene interface.

ethylbenzene interface. The interfacial viscosity of this system is zero. On the other hand, the same Methocel 60 HG in water at an ethylene dichloride interface exhibits a high interfacial viscosity. We believe this point is very significant in formulating a theory concerning interfacial behavior of polymeric surfactants. The explanation probably lies in the relative solubility of the Methocel at the water and oil interface.

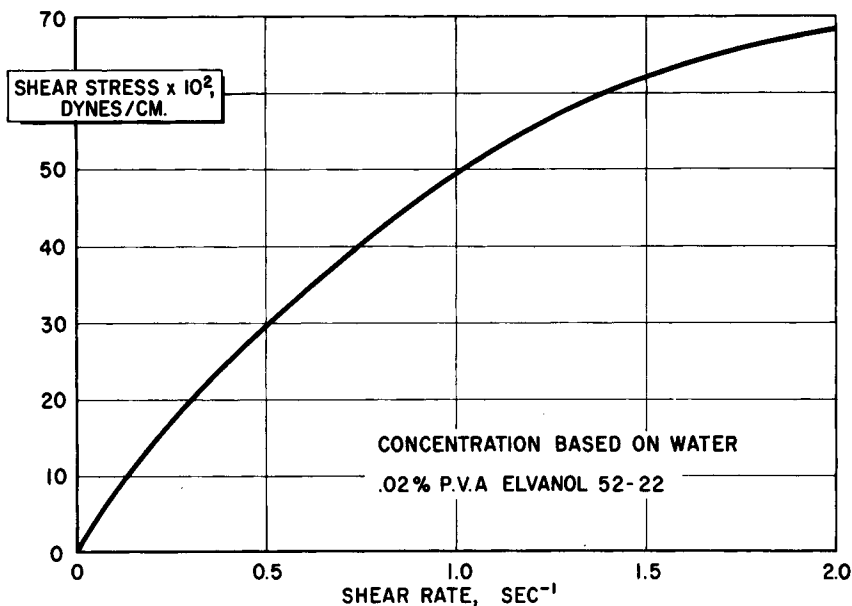


Fig. 7. Rheogram of PVA at water-ethylbenzene interface.

Poly(vinyl Alcohol) (PVA)

The poly(vinyl alcohol) used in this study was Elvanol 52-22. Figure 7 shows a typical poly(vinyl alcohol) rheogram. PVA has markedly different rheological properties than methylcellulose. It is not rigid, elastic, or brittle. It is a pseudoplastic, contrasted to methylcellulose which has a Bingham or plastic type of rheological behavior.

Polymer of Diethylene Glycol n-Butyl Ether Acrylate

Figure 8 shows the rheogram of this acrylate polymer. This material exhibited Newtonian rheological behavior. The interfacial viscosity of 0.02% concentration was 0.92×10^{-2} surface poise.

The data presented in Figures 3-8 illustrates the complexity of polymeric surfactants and the importance of studying their rheological behavior over a wide range of shear rates. It should be emphasized that the four polymeric surfactants studied all exhibited Newtonian flow properties in the bulk solution. Furthermore, the bulk solution viscosity was not much different from that of water.

The interfacial viscosity, as noted in Figures 3-8, is a small value. However, if we take into account the thickness of the film, the interfacial viscosity represents a highly viscous interface.

Effect of Temperature

Figure 9 shows a plot of interfacial yield stress as a function of temperature for two types of Methocel, MC Premium and Methocel 90 HG. At

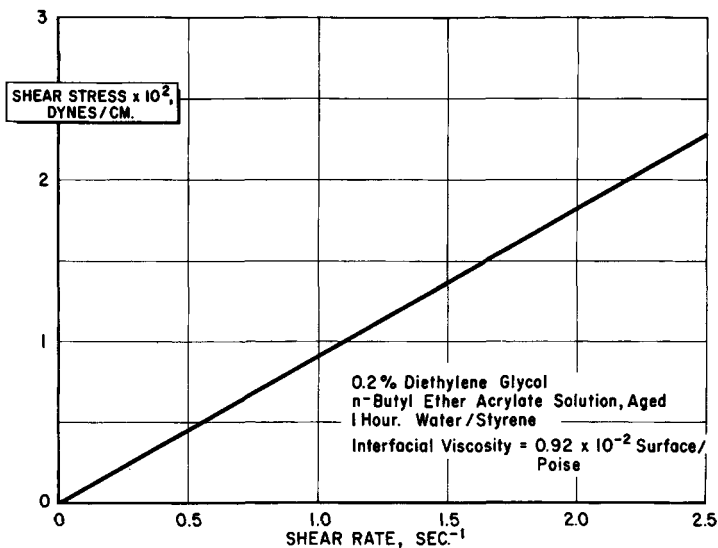


Fig. 8. Interfacial film rheogram.

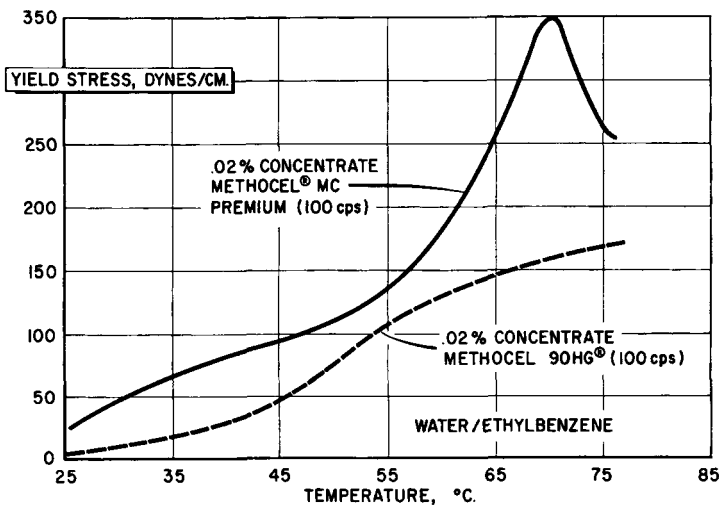


Fig. 9. Effect of temperature on yield stress.

70°C, the yield stress decreases sharply for the Methocel MC Premium (100 cps). It is assumed that this is the gelation temperature of this type of Methocel at this concentration. The Methocel 90 HG, since it has a higher gelation temperature, did not exhibit any marked drop in yield stress at the elevated temperature. The increase of interfacial viscosity with temperature indicates that molecules of the absorbed film at the interface become more extended and hence form a more effective film. Surface coverage data, which will be discussed later, substantiate this conclusion.

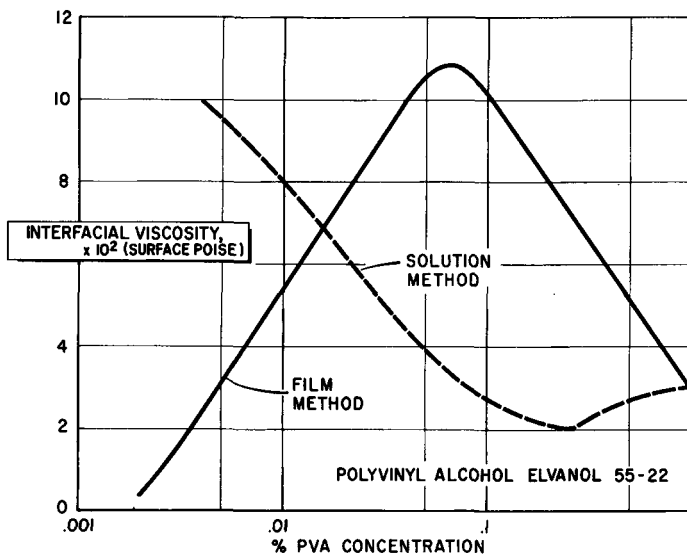


Fig. 10. Effect of concentration on interfacial viscosity.

All polymeric surfactants did not exhibit an increase in viscosity with an increase in temperature. For example, sulfonated poly(vinyltoluene) exhibited a decrease in interfacial viscosity with an increase in temperature.

The bulk viscosity of the solutions studied all exhibited a decrease in viscosity with an increase in temperature. This again points out the fact that interfacial films, especially of polymeric material, possess complex rheological properties which are much different than their bulk properties.

Effect of Concentration

The effect of concentration on interfacial viscosity was not a simple relationship as in bulk solution properties. Figure 10 shows a typical result obtained with poly(vinyl alcohol). Similar behavior has been observed with methylcellulose. We do not have any logical explanation for the behavior observed.

Figure 10 illustrates the type of data that can be obtained by the two techniques described earlier for obtaining interfacial viscosity data. A possible explanation for the difference in the curves observed is that by the use of film technique equilibrium is attained quickly at the interface. It has the disadvantage in that molecules of the surfactant in the added layer could diffuse from the interface to the bulk liquid phase. Given enough time, equilibrium concentration would be attained at the interface. Although not a proven fact, we are of the opinion that given enough time, the two curves would coincide.

Effect of Additives

Interfacial films can be plasticized. Figure 11 illustrates how a brittle methylcellulose film can be made ductile by the addition of Duponol ME,

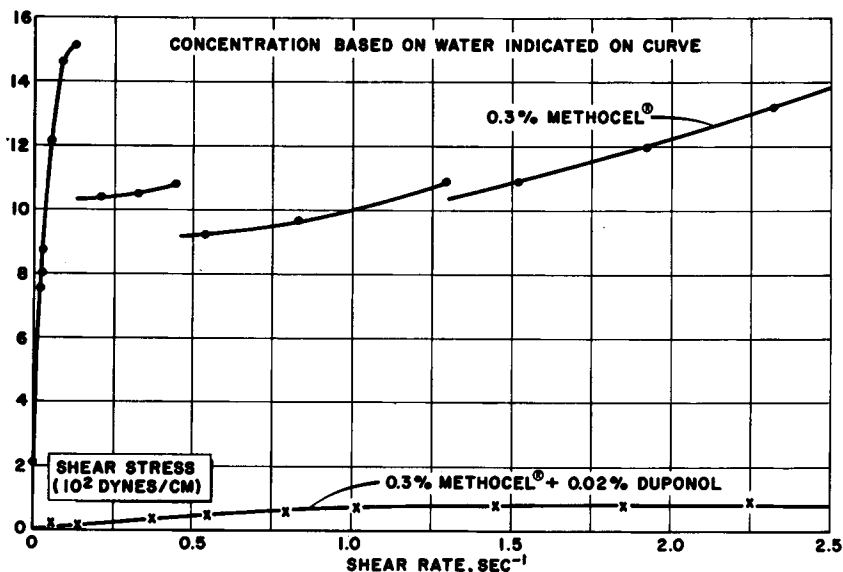


Fig. 11. Rheogram of Methocel and Duponol at water-ethylbenzene interface.

sodium lauryl sulfate. The plasticization of film is important from a practical viewpoint. This will be discussed in detail in a later portion of the report.

Specific Area Measurement

The interfacial viscometer lends itself to measuring the specific area of a surfactant, defined as the amount of effective coverage per unit weight of material. There are a number of techniques that have been used to determine this property. They are discussed in references 2, 4, and 5. The classical method involves the use of the surface pressure balance, sometimes referred to as the "Langmuir balance." The chief disadvantage of this instrument is that it does not lend itself to interfacial measurements. Because of this limitation, we compared the results obtained by the interfacial viscometer with those obtained by the "interfacial tension technique or ring method."

The "interfacial viscometer technique" for measuring specific areas consisted of measuring a rheological property of a film as a function of concentration. A fixed amount of solutions of various concentrations was floated at the interface, by the second technique described earlier. The interfacial yield was then measured. Figure 12 shows a typical result obtained with methylcellulose. By definition, the point at which the curve began to concave upward was the specific area coverage of the film.

Investigators have stressed theoretical significance of the shape of surface pressure versus concentration curves.² Probably similar arguments can be advanced regarding surface viscosity-versus-concentration curves. We have obtained curves similar to "condensed," "expanded," and "gaseous" films, as observed with surface pressure measurements.

Table I summarizes the values for surface coverage of the four types of polymeric surfactants. Results were obtained by two methods and com-

TABLE I
Surface Area Coverage (cm²/g)^a

Material	Interfacial viscosity	Ring method	Calculated value
Methylcellulose (Methocel MC Premium 100 cps.)	3.8×10^6	4.0×10^6	2.75×10^6
Poly(vinyl alcohol) (Elvanol 52-22)	1.2×10^6	1.2×10^6	1.85×10^6
Polymer of diethyl glycol <i>n</i> -butyl ether acrylate	0.26×10^6	0.22×10^6	
Sulfonated poly(vinyl- toluene)	0.07×10^6	0.07×10^6	

^a Temperature 25°C.

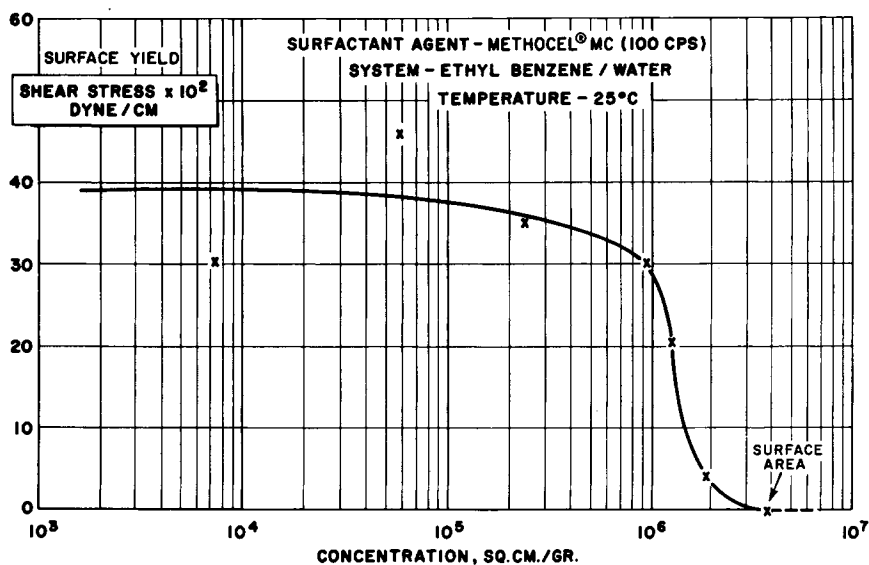


Fig. 12. Plot of surface yield vs. concentration.

pared with a theoretical value calculated on the basis of x-ray data of the unit molecular cell and assumed ordered packing. Note that for methylcellulose and poly(vinyl alcohol), the experimental value was a factor of 10 larger than the calculated value. It is possible that the discrepancy lies in the assumptions made in the calculations. We propose that the explanation lies in the fact that the polymeric surfactant forms an irregular film at an interface. If ordered packing had occurred, the experimental value would have agreed with the calculated value.

SIGNIFICANCE OF INTERFACIAL VISCOSITY WITH RESPECT TO EASE OF DROPLET BREAKUP

It has been hypothesized that methylcellulose forms a coherent film about hydrocarbon droplets. The film can resist the viscous forces that tend to deform a liquid droplet in a shear field.

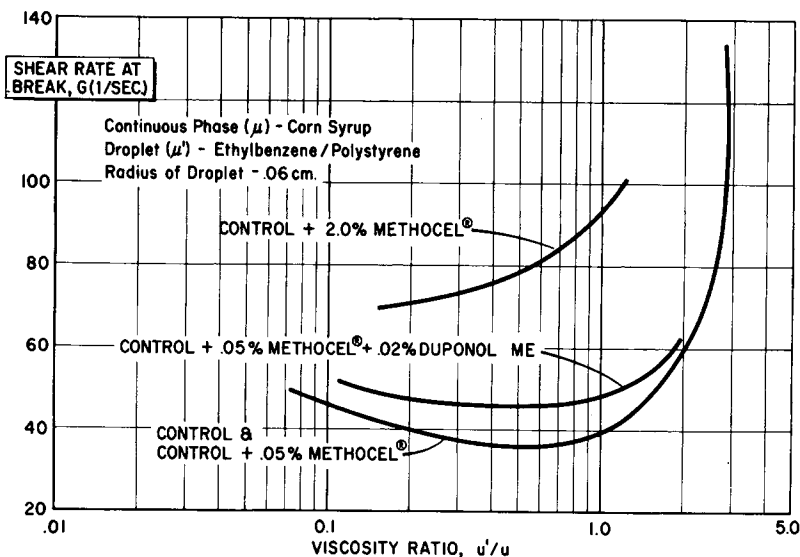


Fig. 13. Droplet breakup.

The effect of an interfacial film on droplet breakup was studied in the apparatus discussed in reference 6. The system studied consisted of corn syrup as the continuous phase and droplets of a solution of polystyrene in ethylbenzene. Experiments consisted of studying breakup with and without methylcellulose added to the corn syrup. Results are summarized in Figure 13. Note that, as expected, the addition of 2% methylcellulose to the corn syrup made it more difficult to break up the polystyrene solution droplets. A surprising result was that the addition of 0.05% methylcellulose to the corn syrup did not alter the breakup pattern. However, the addition of Duponol ME to the corn syrup-methylcellulose solution made it more difficult to break up the polystyrene solution droplets. The addition of Duponol ME should have made it easier to break up the droplets since it lowered the interfacial tension. The lower interfacial tension was offset by the increased effectiveness of the methylcellulose, as a protective colloid, by the addition of the Duponol ME. This point was discussed previously when it was shown that interfacial film of methylcellulose was plasticized by the addition of Duponol ME.

Similar results to those observed with methylcellulose were observed with sulfonated poly(vinyltoluene) as a surfactant. As in the methylcellulose study, the addition of Duponol ME to SPVT increased the difficulty of breaking up the polystyrene solution droplets.

A theoretical discussion of how an absorbed film at an interface effects droplet breakup is given in references 7 and 8. We have not applied the theory to our observations, primarily because it requires additional physical parameters to describe the nature of the absorbed film. These additional parameters have not been determined for the polymeric surfactants studied.

The experimental and theoretical results of the liquid droplet breakup substantiates the hypothesis that polymeric surfactants absorb at interfaces

and form films that possess complex rheological behavior. Similar conclusions can be deduced in the study of stabilization of suspensions and emulsions.

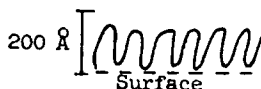
CONCLUSIONS

1. The surface viscometer described can be used to obtain rheological properties of polymeric surfactants at liquid-liquid or liquid-air interfaces.
2. Interfacial films of polymeric surfactants at liquid-liquid interface have complex rheological properties.
3. Interfacial viscosities are a complex function of temperature and concentration of surface active materials.
4. Interfacial films can be plasticized.
5. Rheological properties of interfacial films will change with time.
6. The interfacial viscometer can be used to obtain critical surface coverage of a surfactant. Results are comparable to those obtained by the ring method.
7. The polymeric films investigated, poly(vinyl alcohol) and Methocel, were irregular, i.e., the polymeric chain is not absorbed in a regular pattern at the interface. In both cases studied, the measured coverage is much greater than can be calculated from x-ray structural data and assumed ordered packing.
8. The addition of a protective colloid around a liquid droplet made it more difficult to break up the droplet in a simple shear field.

Appendix

Calculation of Theoretical Coverage of Methylcellulose

1. Molecular cross section of 32 \AA^2 (from crystal structure data).⁹ Figure 14 shows a diagrammatic representation of the unit cell of native cellulose.
2. Molecular length of 3100 \AA ⁹ (from mean of 600 units of mass 182 per molecule, each unit 5.15 \AA long from crystal structure data).
3. Molecule is folded into segments 200 \AA long (from knowledge of behavior of other polymeric molecules, i.e., polyethylene and polypropylene) so that the average molecule has $3100/200 = \sim 16$ folds, each of which covers an area of 32 \AA^2 , so that the molecule covers an area of $32 \times 16 = \sim 500 \text{ \AA}^2$.



4. There are N molecules per mole, which has a mass of $182 \times 600 \text{ g}$. Thus, each individual molecule has mass $182 \times 600/N \text{ g}$. N is Avagadro's number, which is equal to 6.023×10^{23} molecules/mole.
5. One mole covers $500 \times N \text{ \AA}^2$ /or, since $1 \text{ cm} = 10^{10} \text{ \AA}$, $500 \times N \times 10^{-16} \text{ cm}^2$. One gram (N molecules) covers

$$\frac{500 \times N \times 10^{-16}}{182 \times 600} = \frac{5.00 \times 10^2 \times 6.023 \times 10^{23} \times 10^{-16}}{1.82 \times 10^2 \times 6.0 \times 10^2} = \frac{5.00 \times 6.023}{1.82 \times 6.00} \\ \times \frac{10^2 \times 10^{23} \times 10^{-16}}{10^2 \times 10^2} = 2.75 \times 10^5 \text{ cm}^2/\text{g} = 275,000 \text{ cm}^2/\text{g}.$$

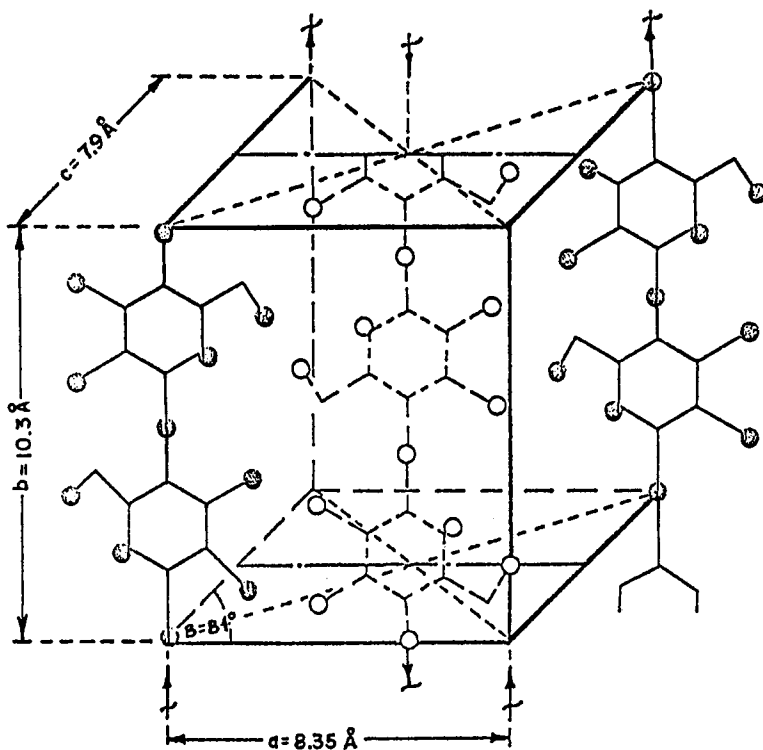
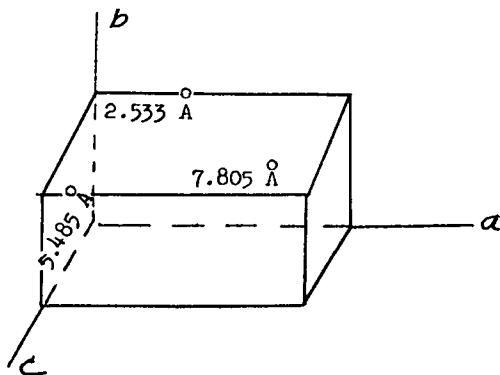


Fig. 14. Diagrammatic representation of the unit cell of native cellulose (Meyer and Misch⁹). Molecular cross section $\sim 32 \text{ \AA}^2$; base area $\sim 64 \text{ \AA}^2$.

Calculation of Theoretical Coverage of Poly(vinyl Alcohol)

Unit crystal of PVA



Two Monomer Units/Cell Ziz Zag Chain

$$a = 7.805 \text{ \AA}$$

$$b = 2.533 \text{ \AA}$$

$$c = 5.485 \text{ \AA}$$

$$\beta = 92.2^\circ$$

density crystalline phase = 1.345

density amorphous phase = 1.269

Molecular axis parallel with crystallographic b axis.

$$\text{area of unit cell} = 43.78 \text{ \AA}.$$

$$\therefore \text{cross-sectional area of molecule} = 21.4 \text{ \AA}^2.$$

1 Calculate number of molecular units:

$$\text{no. of units} = \frac{\text{Molecular Weight of Polymer}}{\text{Molecular Weight of Monomer}}$$

$$\text{no. of units} = \frac{148,000^*}{44} = 3,370 \text{ units (*From du Pont Tech. Bulletin)}$$

2. Calculate length of molecule:

$$\text{size per molecule} = \frac{2.533 \text{ \AA}}{2} = 1.266 \text{ \AA}$$

$$\text{length} = \text{units} \times 1.266 \text{ \AA} = 3,370 \times 1.266 \text{ \AA} = 4,270 \text{ \AA}$$

3. Calculate the number of folds. Assume 200 \AA length per fold:

$$\text{no. of folds} = \frac{4,270}{200} \sim 21 \text{ folds}$$

4. Area covered by each molecule is then equal to $21 \times 21.4 \text{ \AA}^2 = 452 \text{ \AA}^2$.

5. There are N molecules per mole which have a mass of $44 \times 3370 \text{ g}$. Each molecule has a mass equal to $44 \times 3370/N \text{ g}$, where N is Avagadro's number, which is equal to 6.023×10^{23} molecules/mole.

$$\text{One gram covers} \frac{452 \text{ \AA}^2 \times N}{44 \times 3370} = \frac{4.52}{4.4} \left| \frac{6.023}{3.37} \right| \frac{10^{-16}}{10^4} \left| \frac{10^{23}}{10^3} \right| = 1.85 \times 10^6 \text{ cm}^2/\text{g}.$$

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