the 5th International Chisa Congress, Prague, Czechoslovakia (1975).

van Goolen, J. T. J., "Development and Scale-up of a Three-Phase Reactor," *Proceedings of the 4th International 16th European Symposium on Chemical Reaction Engineering,* pp. 399-407, Heidelberg, Germany (1976).

van Swaaij, W. P. M., J. C. Charpentier, and J. Villermaux, "Residence Time Distribution in the Liquid Phase of Trickle Flow in Packed Columns," *Chem. Eng. Sci.,* 24, 1083 (1969).

Vergnes, F., "A Simple and Practical Method for the Determination of the Peclet Number in the Longitudinal Dispersion Model," *ibid.,* 31, 88 (1976).

Volpicelli, G., and L. Massimilla, "Three Phase Fluidized Bed Reactors: An Application to the Production of Calcium Bi-Sulfite Acid Solutions," *ibid.,* 25, 1361 (1970).

von Kutepow, N., W. Himmele, and H. Hohnschutz, "Die Synthese von Essigraure aus Methanol und Koblenoxy," *Chemie-Ing. Techn.,* 37, 383 (1965).

Watson, J. S., and L. McNeese, "Axial Dispersion in Packed Columns During Countercurrent Flow," *Ind. Eng. Chem. Process Design Develop.,* **11,** No. 1, 120 (1972).

Wen, C. Y., and L. T. Fan, "Models for Flow Systems and Chemical Reactors," *Chemical Processing and Engineering Monograph Series,* Dekkar, New York (1975).

Whalley, P. B., and J. F. Davidson, "Liquid Circulation in Bubble Columns," Proceedings of the Symposium on Multiphase Flow Systems, Symposium Series No. 38 (1975).

Woodburn, E. T., "Gas Phase Axial Mixing at Extremely High Irrigation Rates in a Large Packed Absorption Tower," *AIChE J.,* **20,** No. 5, 1003 (1974).

Yagi, S., and T. Miyauchi, "Operational Characteristics of the Continuous Flow Reactors n which the Reactants are Mixing," *Chem. Eng. J.,* **19,** 507 (1955).

Yamagishi, K., O. Kageyama, H. Haruki, and Y. Numa, "Make Propylene Oxide Direct," *Hydrocarbon Process.,* **55,** No. 11, 102 (1976).

Zuiderweg, F. J., and C. Bruinzeel, C., "Liquid Mixing and Oscillations in Sparged Horizontal Cylindrical Vessels," *Proceedings of the 4th European Symposium on Chemical Reaction Engineering,* Supplement to Chemical Engineering Science, p. 183 (1968).

Manuscript received June 6, 1977; revision received December 21, and accepted January 5, 1978.

A Constitutive Equation for a Viscoelastic Interface

J. W. GARDNER
J. V. ADDISON
and
R. S. SCHECHTER

Department of Chemical Engineering
The University of Texas at Austin
Austin, Texas 78712

A constitutive equation has been developed to relate surface stresses to the deformational history of an interface. This equation is designed to provide a unified description of complex interfacial rheological phenomena. New and as yet unreported behavior such as surface normal stresses and viscoelastic contributions to the dynamic surface tension are predicted.

A monolayer of poly(vinyl alcohol) adsorbed at an air/water interface has been studied using a deep channel surface rheometer and the observed viscoelastic behavior shown to be fitted by the model.

SCOPE

Surface active molecules preferentially adsorb at an interface, often forming a dense, packed monolayer even though the concentrations in the adjacent bulk phases are quite small. The presence of small quantities of surfactants may not measurably change the bulk rheological properties, but mechanical properties may be altered dramatically in the interfacial region. For example, it is possible for the surface viscosity to exhibit shear-rate dependence even though the bulk phases may be Newtonian. Also, viscoelastic behavior in which the surface tends to snap back upon relaxation of stress has been observed. It is the purpose of this paper to unify such phenomena.

The mechanical behavior of bulk phases has, in general, been described through the use of constitutive equations, or rheological equations of state, which contain parameters whose values depend on the nature of the fluid. A parallel approach is taken here. A constitutive equation which applies to the interfacial region is presented. This equation allows for both non-Newtonian steady shear and viscoelastic behavior and therefore provides a unified description of complex interfacial rheological phenomena. Since the constitutive equation contains a number of parameters, it is reasonable to inquire as to whether or not these parameters are experimentally accessible, and, if they are, does the equation represent a real fluid interface. To demonstrate that at least some real surfaces can be represented by the proposed equation, the interfacial behavior of an aqueous solution of poly(vinyl alcohol) has been studied. To evaluate the parameters, a new experimental technique which employs a small amplitude sinusoidal surface deformation has been used in conjunction with surface viscometry. The data are closely approximated by the constitutive equation.

Viscoelastic interfaces have previously been represented using simple rate-type constitutive equations, which contain one or more partial derivatives with respect to time but not more complicated frame indifferent (Astarita and Marrucci, 1974) time derivatives. The Maxwell model (Joly, 1972; Mannheimer and Schechter, 1970) is one example.

Shear-rate dependent surface viscosities (one type of non-Newtonian steady shear behavior) have been treated using generalized Newtonian constitutive equations (Astarita and Marrucci, 1974), where the stress may be a nonlinear function of strain rate but not of the deformational history. The Powell-Eyring model has, for example, been used (Pintar, Israel, and Wasan, 1971). Both the

---

J. W. Gardner is with the Shell Development Company, 3737 Bellaire Blvd., Houston, Texas 77025.

0001-1541-78-1021-0400-$00.95.

generalized Newtonian and simple rate-type of constitutive equations are limited in applicability, the former to steady shear and the latter to small deformational flows. The model presented here applies to both of these flows as well as to nonsteady, large deformational flows. The model can thus be used to relate different surface rheological experiments involving an interface having a fading memory (a viscoelastic interface). It may also be useful in determining appropriate boundary conditions for the equation of motion.

CONCLUSIONS AND SIGNIFICANCE

The constitutive equation presented in this paper is the first one proposed which has the capability of representing complex viscoelastic surfaces. The model predicts a number of interesting phenomena, some of which have yet to be experimentally confirmed. For example, surface normal stresses, not considered before, are predicted. Furthermore, the dynamic surface tension of a viscoelastic interface is characterized.

Finally, a special case of the constitutive equation containing six parameters is proposed and some of its consequences presented. Studies of an adsorbed poly(vinyl alcohol) film have been conducted in a deep channel surface rheometer and the observed behavior found to be well correlated by the six-parameter model.

MOMENTUM BALANCES

The mathematical statement of conservation of momentum in a two-phase system provides a boundary condition wherein the rheological behavior of the interface is introduced. The equation which governs the motion of each bulk phase and with which the boundary condition is associated is (Bird, Stewart, and Lightfoot, 1960)

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P - \nabla \cdot \underline{\boldsymbol{\tau}} + \rho \mathbf{g} \tag{1}$$

The boundary condition is (Scriven, 1960; Slattery, 1964, 1967)

$$\mathbf{N}(P^{I} - P^{II}) + \mathbf{N} \cdot (\boldsymbol{\tau}^{I} - \boldsymbol{\tau}^{II}) = - 2\, H\sigma \mathbf{N} - \nabla_s \sigma + \nabla_s \cdot \boldsymbol{\tau}^{s} \tag{2}$$

and applies at the interface.

Since the constitutive equation developed here applies to fluid interfaces, and since only fluid bulk phases are considered, necessary conditions for mechanical equilibrium are that

$$\boldsymbol{\tau} = 0 \tag{3}$$

and

$$\boldsymbol{\tau}^{s} = 0 \tag{4}$$

In particular, if these conditions are applied to Equation (2), the normal component of that equation reduces to the LaPlace equation which defines the pressure jump across an interface. This paper is, of course, concerned with nonequilibrium situations ($\boldsymbol{\tau}^{s} \neq 0$).

THE SURFACE CONSTITUTIVE EQUATION

The model presented here is basically a modified, two-dimensional version of a constitutive equation developed by Tanner and Simmons (1967) for incompressible, viscoelastic, bulk phases. However, the present model is not limited to incompressible interfaces.

The equation has the following form:

$$\underline{\boldsymbol{\tau}}^{s} = \int_0^\infty \left\{ M(s,\psi)\underline{\mathbf{L}}(s) + \frac{K(s,\psi) - M(s,\psi)}{2}\, tr\underline{\mathbf{L}}(s)\, \underline{\mathbf{1}}_s \right\} ds \tag{5}$$

where $M(s,\psi),\ K(s,\psi) = \begin{cases} m(s),\ k(s) & \text{if } \psi \leq B^2 \\ 0 & \text{if } \psi > B^2 \end{cases},$

and $m(s)$, $k(s)$ = memory functions which decay with s.

In simple terms, the model describes an interface whose memory fades with time but is also limited to deformations of a certain magnitude, namely, those for which $\psi \leq B^2$.

Equation (5) is a complex equation, and the predicted flow behavior obtained by introducing it into the boundary condition is not readily discernable. However, it should be noted that this is the only general constitutive equation which has been proposed for an interface. Its true usefulness can only be assessed by comparing predicted with observed behavior.

STEADY SHEAR SURFACE FLOWS

Let us consider a flat interface lying in the x-y plane of a Cartesian coordinate system x, y, z. Suppose that the motion in the interface is such that

$$v_x = v_x(y) \tag{6}$$
$$v_y = 0$$

For this steady shear surface flow [for a more general statement of steady shear surface flows see Gardner (1975)], the model predicts that

$$\tau^{s}_{xy} = -\eta(\dot{\gamma})\frac{dv_x}{dy} \tag{7}$$

where the steady shear surface viscosity $\eta(\dot{\gamma})$ is given by

$$\eta(\dot{\gamma}) = \int_0^{B/\dot{\gamma}} s\, m(s)\, ds \tag{8}$$

Note that η depends on the surface shear rate $\dot{\gamma}$ $\left(\dot{\gamma} = \left|\frac{dv_x}{dy}\right|\right)$; that is, the film is non-Newtonian.

A careful analysis of steady shear flow reveals the predicted existence of surface normal stresses. No mention of this possibility has been suggested in the literature, although in some of our studies using the deep channel surface viscometer (Burton and Mannheimer, 1967; Mannheimer and Schechter, 1970a) we have observed behavior which may very well be attributed to the existence of surface normal stresses. The model predicts that for the steady shear flow above

$$-\tau^s_{xx} = \tau^s_{yy} = \theta(\dot{\gamma}) \left(\frac{dv_x}{dy}\right)^2 \tag{9}$$

where the normal stress coefficient θ is given by

$$\theta(\dot{\gamma}) = 1/2 \int_o^{B/\dot{\gamma}} s^2\, m(s)\, ds \tag{10}$$

No experiment has yet been reported quantitatively establishing the existence of surface normal stresses; however, using Equation (10) in conjunction with a six-parameter model proposed in a subsequent section, the magnitude of the effect can be estimated assuming, of course, that the model is representative of the real system.

SMALL DEFORMATIONAL SURFACE FLOWS

For any small deformational surface flow (whether shear, dilational, compressional, or a combination thereof), the model reduces to

$$\underline{\boldsymbol{\tau}}^s = \int_0^\infty \left\{ m(s)\underline{\mathbf{G}}(s) + \frac{k(s) - m(s)}{2}\, tr\underline{\mathbf{G}}(s)\underline{\mathbf{1}}_s \right\} ds \tag{11}$$

As an example of a small deformational surface flow, consider a plane, sinusoidal shear of small amplitude. Again, suppose the interface lies in the x-y plane of a Cartesian coordinate system x, y, z. But this time suppose that

$$v_x = Im\{v^*(y)e^{i\omega t}\} \tag{12}$$

$$v_y = 0 \tag{13}$$

where $v^*(y)$ = a complex function of y, $i = \sqrt{-1}$, and $Im\{\ \}$ = imaginary component. For this type of surface flow [for a more general type of small amplitude sinusoidal shear surface flow, see Gardner (1975)], the model predicts that

$$\tau^s_{xy} = -Im\left\{ \eta^*(\omega)\, \frac{dv^*}{dy}\, e^{i\omega t} \right\} \tag{14}$$

$$\tau^s_{xx} = \tau^s_{yy} = 0 \text{ (approximately)} \tag{15}$$

where

$$\eta^*(\omega) = \text{complex surface viscosity}$$

$$= \eta' - i\left(\frac{G'}{\omega}\right) \tag{16}$$

$$\eta'(\omega) = \text{dynamic surface viscosity}$$

$$= \int_0^\infty \frac{m(s)\sin(\omega s)}{\omega}\, ds \tag{17}$$

$$G'(\omega) = \text{dynamic surface rigidity}$$

$$= \int_0^\infty m(s)\,[1 - \cos(\omega s)]\, ds \tag{18}$$

Note that the material functions $\eta(\dot{\gamma})$, $\theta(\dot{\gamma})$, $\eta'(\omega)$, and $G'(\omega)$ are all related through the shear memory function $m(s)$. This memory function can, in principle, be evaluated by measuring the complex viscosity as a function of frequency and performing an inverse Fourier transform. However, an easier procedure is to define $m(s)$ by an approximate functional form and to evaluate those parameters which are dependent on the nature of the interfacial film using experimental data. This approach will be demonstrated in a subsequent section.

DILATIONAL AND COMPRESSIONAL SURFACE FLOWS

The constitutive equation yields some interesting predictions for dilational and compressional surface flows. These may be seen as follows. For any nonshearing surface flow and independent of the magnitude of the deformation, Equation (5) takes the form

$$\boldsymbol{\tau}^s = -\Delta\sigma_d\, \mathbf{1}_s \tag{19}$$

where

$$\Delta\sigma_d = 1/2 \int_0^\infty K(s, \psi) \left\{ \frac{1}{J(s)} - J(s) \right\} ds \tag{20}$$

and $J(s)$ is the ratio of the specific surface area at time $t - s$ to that at time t. Thus, in a dilational or compressional surface flow, the dynamic surface tension is equal to the equilibrium value σ plus a dynamic contribution $\Delta\sigma_d$. In a dilational case, where $J(s) < 1$, $\Delta\sigma_d$ is positive, and the effective surface tension is larger than the equilibrium value.

On the other hand, a film being compressed will exhibit an apparent surface tension less than the equilibrium value, since here $J(s) > 1$.

As an example of a dilational surface flow, consider a spherical interface which has expanded at a constant rate dr/dt to get to its present radius r. Here, the model predicts that

$$\Delta\sigma_d = 1/2 \int_o^{s_e} k(s) \left\{ \left[\frac{1}{1 - s\frac{dr/dt}{r}} \right]^2 - \left(1 - s\frac{dr/dt}{r}\right)^2 \right\} ds \tag{21}$$

where s_e satisfies

$$s_e = \frac{1 - \left\{ \dfrac{1}{2 + B^2 - \left(1 - s_e \dfrac{dr/dt}{r}\right)^2} \right\}^{1/2}}{\dfrac{dr/dt}{r}} \tag{22}$$

[A situation where $1 - \dfrac{s_e(dr/dt)}{r} \leqq 0$ is, of course, nonphysical.]

If, on the other hand, a spherical interface has contracted at a constant rate to get to its present radius (a compressional surface flow), the model predicts that

$$\Delta\sigma_d = 1/2 \int_0^{s_c} k(s) \left\{ \left[\frac{1}{1 + s\left|\frac{dr/dt}{r}\right|} \right]^2 - \left(1 + s\left|\frac{dr/dt}{r}\right|\right)^2 \right\} ds \tag{23}$$

where s_c satisfies

$$s_c = \frac{\left\{ 2 + B^2 - \left[\dfrac{1}{1 + s_c\left|\dfrac{dr/dt}{r}\right|} \right]^2 \right\}^{1/2}}{\left|\dfrac{dr/dt}{r}\right|} \tag{24}$$

While experiments to verify these predictions have not been carried out, it is clear that they may have significance in processes where bubbles are entrained in a moving liquid stream and surface active materials are present.

MEMORY FUNCTIONS

To apply the model in an arbitrary flow situation, shear and dilatory memory functions $m(s)$ and $k(s)$ containing a finite number of parameters which depend only on the composition of the interface are required. (Recall that the model already contains one parameter B.) We give here an example of a shear memory function only; namely

$$m(s) = \frac{\delta(s)}{s}\eta_\infty + \sum_{n=1}^{\infty} \frac{\mu_n}{\lambda_n^2} e^{-s/\lambda_n} \tag{25}$$

where

$\delta(s)$ = Dirac delta function

$$\mu_n = (\eta_0 - \eta_\infty) \frac{\left(\frac{2}{n+1}\right)^\alpha}{\sum_{p=1}^{\infty}\left(\frac{2}{p+1}\right)^\alpha} \tag{26}$$

$$\lambda_n = \lambda\left(\frac{2}{n+1}\right)^\beta \tag{27}$$

α, β, λ, η_0, and η_∞ are parameters which depend on the composition of the interface but not on the deformational history. Equation (25) is taken from Tanner and Simmons (1967) and Equations (26) and (27) from Bird and Carreau (1968). The result is a five-parameter memory function appropriate to shear thinning, viscoelastic interfaces.

The following material functions result from the combination of Equation (25) and Equations (8), (10), (17), and (18):

$$\eta(\dot\gamma) = \eta_\infty + \sum_{n=1}^{\infty} \mu_n \left\{ 1 - \left(1 + \frac{B}{\lambda_n\dot\gamma}\right) e^{-\beta/\lambda_n\dot\gamma} \right\} \tag{28}$$

$$\theta(\dot\gamma) = \sum_{n=1}^{\infty} \mu_n\lambda_n \left\{ 1 - \left(1 + \frac{B}{\lambda_n\dot\gamma} + \frac{B^2}{2\lambda_n^2\gamma^2}\right) e^{-B/\lambda_n\dot\gamma} \right\} \tag{29}$$

$$\eta'(\omega) = \eta_\infty + \sum_{n=1}^{\infty} \frac{\mu_n}{1 + \lambda_n^2\omega^2} \tag{30}$$

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} = \sum_{n=1}^{\infty} \frac{\mu_n\lambda_n\omega}{1 + \lambda_n^2\omega^2} \tag{31}$$

Figure 1 illustrates the shear rate and frequency dependence of $\eta(\dot\gamma)$ and $\eta^*(\omega)$ (in terms of η' and η'') predicted by the six-parameter model for four hypothetical films whose properties are defined in Table 1. Relatively speaking, film A has a small surface viscosity (small η_0 and η_∞) and long memory (or large relaxation time, λ), film B a small surface viscosity and short memory, film C a large surface viscosity and short memory, and film D a large surface viscosity and long memory.

Relationships completely analogous to Equations (28), (30), and (31) can be found in Tanner and Simmons (1967). [A relationship somewhat similar in appearance to Equation (29) but having different physical significance also appears in Tanner and Simmons (1967)]. If we use Equations (28) to (31), the applicability of the constitutive equation, at least the special case associated with Equation (25), can be tested.

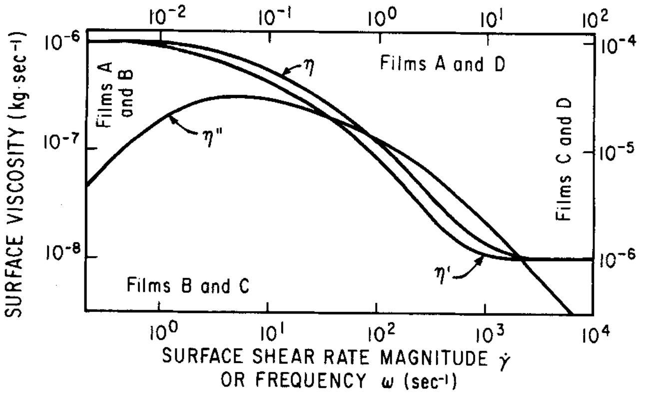

Fig. 1. Four six-parameter films [material functions $\eta(\gamma)$ and $\eta^*(\omega)$ vs. $\dot\gamma$ and ω, respectively].

TABLE 1. FOUR HYPOTHETICAL SIX-PARAMETER FILMS AND EXPERIMENTALLY DETERMINED PARAMETERS FOR POLY(VINYL ALCOHOL)

Film	η_0(kg · s^{-1}) × 10^6	η_∞(kg · s^{-1}) × 10^8	λ(s)	α(—)	β(—)	B(—)
A	1.0	1.0	50.0	1.56	1.88	2.5
B	1.0	1.0	0.5	1.56	1.88	2.5
C	100.0	100.0	0.5	1.56	1.88	2.5
D	100.0	100.0	50.0	1.56	1.88	2.5
Poly(vinyl-alcohol)	55.0	991.0	7.99	1.75	1.69	15.0

Gardner and Schechter (1976) have proposed a method of evaluating the six parameters α, β, λ, η_0, η_∞, and B using data obtained from the deep channel surface rheometer (Burton and Mannheimer, 1967; Mannheimer and Schechter, 1970a) modified so that the floor can be made to oscillate at varying frequencies as well as rotate continuously as was originally suggested. In both cases, the device consists of a moving floor bounded by fixed walls as depicted in Figure 2. The actual geometry of the system is an annular one as shown. However, it has been shown that the annular geometry can be assumed to be linear if the rheometer is properly designed (Mannheimer and Schechter, 1968). Furthermore, under certain conditions the gap between the movable floor and stationary walls as well as the meniscus can be neglected (Pintar, Isreal, and Wasan, 1971). In the analysis to follow, it is assumed that these conditions apply.

For the steady shear experiments, the floor is made to rotate at a constant velocity and measurements consist of determining the rotation period of a particle carefully

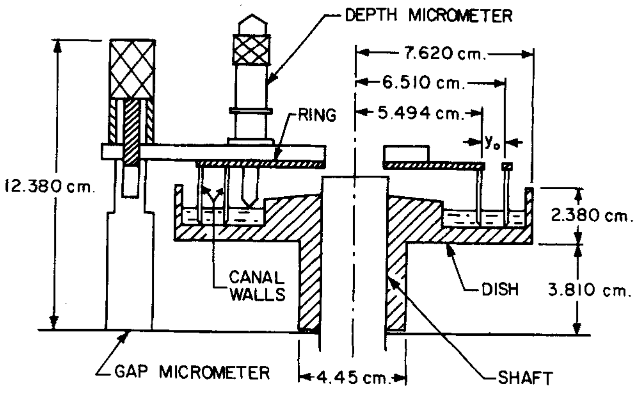

Fig. 2. Deep channel surface viscometer.

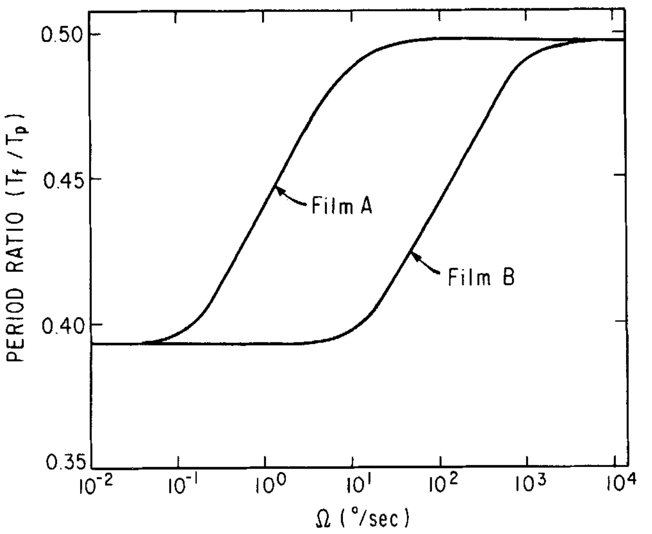

Fig. 3. Period ratio vs. Ω (films A,B).

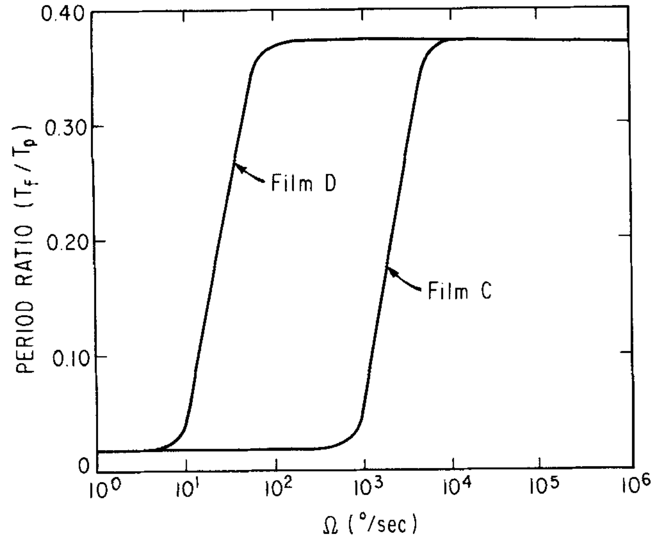

Fig. 4. Period ratio vs. Ω (films C,D).

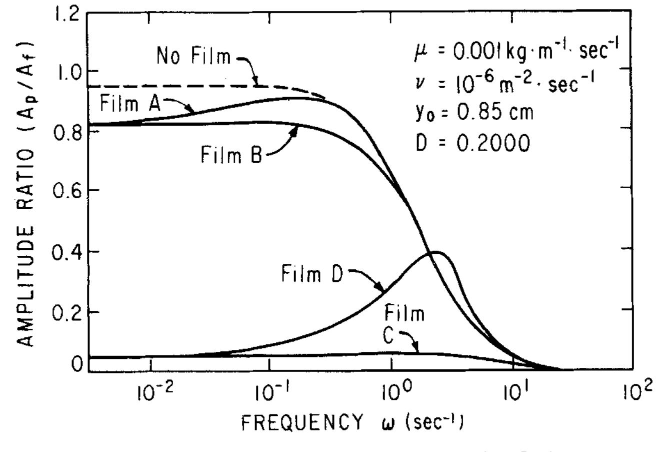

Fig. 5. Amplitude ratio vs. frequency (films A,B,C,D).

placed at the surface center line. Figure 3 illustrates how the period ratios (T_f/T_p) for films A and B of Table 1 vary as functions of the rotational speed of the floor for the viscometer used in this study (Figure 2). These curves assume that secondary flow effects are negligible (Gardner and Schechter, 1976). The quantity D is the ratio of liquid depth to annular spacing. The curves are interesting in that the period ratio at low shear rates is that of a Newtonian film having a surface viscosity η_0. At high shear rates, the surface viscosity η_∞ dominates this pseudo plastic behavior. Since films A and B have the same values of η_0 and η_∞, the limiting period ratios are the same. The shear rate at which the transition takes place is governed by the ratio B/λ. Since the relaxation times for films A and B differ by a factor of 100, and B is kept constant, the rotational speed at which the transition takes place also differs by roughly this same factor.

Figure 4 shows similar results for films C and D of Table 1.

If the floor is made to oscillate sinusoidally, the amplitude of a particle at the surface center line can be measured. Figure 5 shows the ratio of the amplitude of the surface to the amplitude of the floor predicted for films A, B, C, and D. The parameters μ and ν are the absolute and kinematic viscosities of the substrate, respectively. For this example, the substrate properties have been selected to roughly correspond to water. Note that the peak for film D is not due to a maximum in the elastic nature of the film at the peak frequency but is a result of the interaction between the hypophase and interface.

These two experiments, steady shear and sinusoidal oscillation, can be used to determine the six parameters. These will depend on the interfacial composition and, of course, on the temperature but should be independent of the particular experiment. An example is provided in the next section.

EXPERIMENTAL RESULTS

A polymeric monolayer adsorbed at an air/water interface has been studied at room temperature. The substrate was an aqueous solution of poly(vinyl alcohol) having an average molecular weight of 10 000 and 88% hydrolyzed (DuPont ELVANOL 50-42). The solution concentration was 0.05 wt.% which corresponds to the critical micelle concentration. The bulk viscosity of this solution was 0.00103 kg · m^{-1} · s^{-1}.

The solutions were introduced into the rheometer channel and allowed to stand for a period of about 8 hr. This time was found experimentally to be sufficient for equilibrium by diffusion.

Figure 6 shows the experimental amplitude ratio as a function of oscillation frequency. Also shown is the result when no film is present. The solid line through the data represents the best fit obtained using a Marquardt modified Gauss-Newton nonlinear regression technique (Kuester and Mize, 1973). Over the frequency range studied, the predicted curve is not sensitive to η_0. The value shown in Table 1 [$\eta_0 = 5.5\ (10)^{-5}$ kg · s^{-1}], was obtained from the steady shear experiment shown in Figure 7.

Since the parameter B does not appear in the formulation of the complex viscosity [Equations (30) and (31)], it must be determined by steady shear experiments. The solid line in Figure 7 shows the best fit of the data obtained by adjusting η_0 and B but using the other parameters best fitting the oscillatory results.

The values of the parameters best representing the data are shown in Table 1. The experimental results are well described by the six-parameter model, thereby demonstrating its utility. Other shearing flows can now be predicted. One example might be a stress relaxation experiment (Mannheimer and Schechter, 1970*b*; Mohan and Wasan, 1976). These preliminary results indicate the potential applicability of the proposed constitutive equation and provide the possibility of a unified approach which can be used to both represent experimental data obtained from a number of different experiments and to predict the

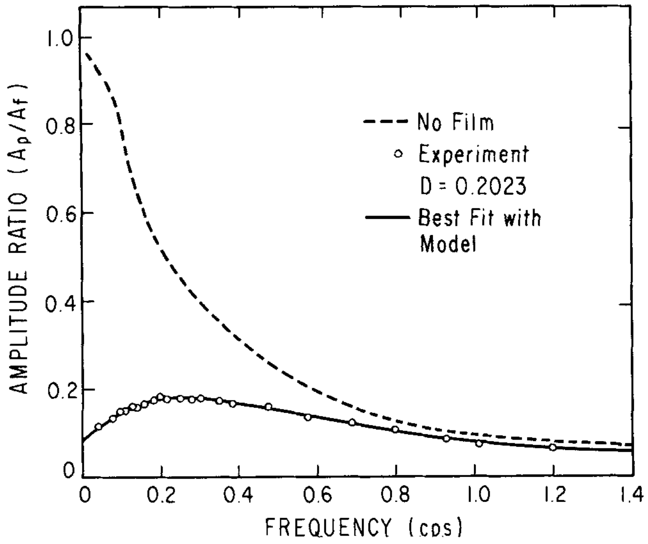

Fig. 6. Ampliaude ratio vs. frequency adsorbed poly(vinyl alcohol).

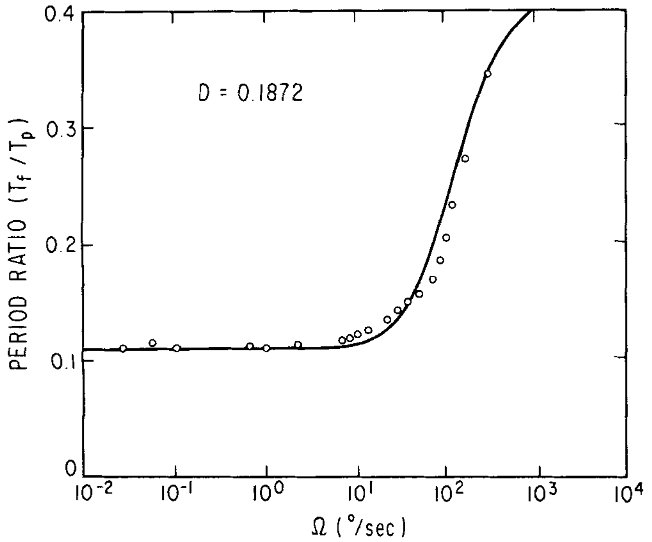

Fig. 7. Period ratio vs. adsorbed poly(vinyl alcohol).

motion of a two-phase system which is to some extent governed by the rheology of the interface.

A subsequent publication will present data demonstrating that the rheological behavior of certain spread monolayers are also described by the model (Addison and Schechter, 1977).

ACKNOWLEDGMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this project. James Addison is a Health, Education and Welfare Fellow.

NOTATION

A_f = amplitude of floor oscillation
A_p = amplitude of surface center-line oscillation
B = model parameter related to the amount of deformation at which the interface loses its memory
D = depth to width ratio
D/Dt = substantial derivative
$\mathbf{g}$ = gravitational vector
$G'(\omega)$ = dynamic surface rigidity
$\mathbf{G}(s)$ = surface analogue of the Cauchy strain tensor
H = mean curvature of the surface
$J(s)$ = ratio of specific surface area at time $t - s$ to that at time t
$k(s)$ = dilatory memory function
$\mathbf{L}(s)$ = surface strain tensor
$m(s)$ = shear memory function
$\mathbf{N}$ = unit normal to the surface
P = pressure
r = radius
s = time into the past
t = present time
T_f = period of floor rotation
T_p = period of surface center-line rotation
$\mathbf{v}$ = velocity

Greek Letters

α = model parameter
β = model parameter
$\dot{\gamma}$ = surface shear rate
∇ = gradient operator
∇_s = surface analogue of the gradient operator
$\eta(\dot{\gamma})$ = steady shear surface viscosity
$\eta^*(\omega)$ = complex surface viscosity
η' = dynamic surface viscosity (real component of the complex surface viscosity)
η'' = imaginary component of the complex surface viscosity
η_0 = model parameter (zero shear rate surface viscosity)
η_∞ = model parameter (infinite shear rate surface viscosity)
λ = model parameter (time constant)
$\theta(\dot{\gamma})$ = surface normal stress coefficient
μ = bulk phase viscosity
ν = bulk phase kinematic viscosity
ρ = bulk phase density
σ = equilibrium surface tension
$\Delta\sigma_d$ = dynamic contribution to the apparent surface tension
$\boldsymbol{\tau}$ = bulk phase stress tensor
$\boldsymbol{\tau}^s$ = surface stress tensor
ψ = an invariant of $\underline{\mathbf{L}}(s)$ associated with the amount of deformation the surface has undergone
Ω = floor rotation rate
ω = frequency
$\mathbf{I}_s$ = surface analogue of the identity tensor

LITERATURE CITED

Addison, J. V., and R. S. Schechter, "An Experimental Study of the Rheological Behavior of Surface Films," submitted to *AIChE J.* for publication (1977).

Astarita, G., and S. Marrucci, *Principles of Non-Newtonian Fluid Mechanics*, McGraw-Hill, New York (1974).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).

Bird, R. B., and P. J. Carreau, "A Nonlinear Viscoelastic Model for Polymer Solutions and Melts—I," *Chem. Eng. Sci.*, **23**, 427 (1968).

Burton, R. A., and R. J. Mannheimer, "Analysis and Apparatus for Surface Rheological Measurements," *Advan. Chem. Ser.*, 63, 315 (1967).

Gardner, J. W., "On the Mechanics of Non-Newtonian Films," Ph.D. dissertation, Univ. Tex., Austin (1975).

———, and R. S. Schechter, "Evaluation of Surface Rheological Models," in *Colloid and Interface Science, Vol. IV: Hydrosols and Rheology*, Milton Kirker, ed., p. 421, Academic Press, New York (1976).

Joly, M., "Rheological Properties of Monomolecular Films," *Surface Collo'd Sci.*, **5**, 1, 79 (1972).

Kuester, J. L., and J. H. Mize, *Optimization Techniques with Fortran*, McGraw-Hill, New York (1973).

Mannheimer, R. J., and R. S. Schechter, "A Comparison of Linear and Annular Canal Viscometers for Surface Rheological Measurements," *J. Colloid Interface Sci.*, **27**, 324 (1968).

——————, "Improved Apparatus and Analysis for Surface Rheological Measurements," *ibid.*, **32**, No. 2, 195 (1970*a*).

——————, "The Theory of Interfacial Viscoelastic Measurement by the Viscous Traction Method," *ibid.*, 225 (1970*b*).

Mohan, B., and D. T. Wasan, "A New Method for the Measurement of Shear Viscoelasticity at Liquid-Liquid Interfaces Containing Surfactant and Monomolecular Films," *Colloid and Interface Science, Vol. IV: Hydrosols and Rheology*, Milton Kirker, ed., p. 439, Academic Press, New York (1976).

Pintar, A. J., A. B. Israel, and D. T. Wasan, "Interfacial Shear Viscosity Phenomena in Solutions of Macromolecules," *J. Colloid Interface Sci.*, **37**, No. 1, 52 (1971).

Scriven, L. E., "Dynamics of a Fluid Interface," *Chem. Eng. Sci.*, **12**, 98 (1960).

Slattery, J. C., "Surfaces—I Momentum and Moment-of-Momentum Balances for Moving Surfaces," *ibid.*, **19**, 379 (1964).

———, "General Balance Equation for a Phase Interface," *Ind. Eng. Chem. Fundamentals*, **6**, No. 1, 108 (1967).

Tanner, R. I., and J. M. Simmons, "Combined Simple and Sinusoidal Shearing in Elastic Liquids," *Chem. Eng. Sci.*, **22**, 1803 (1967).

APPENDIX

Some of the kinematical quantities associated, directly or indirectly, with the model are defined here. Let

$\mathbf{r}$ = position at the present time t of an arbitrary point on the interface

$\mathbf{X}(s, \mathbf{r})$ = position at time $t - s$ of the material point whose position at time t is $\mathbf{r}$

A surface deformation tensor $\mathbf{C}$ can be defined by

$$\mathbf{C} = (\nabla_s \mathbf{X}) \cdot (\nabla_s \mathbf{X})^T$$

$\mathbf{C}$ is the surface analog of the Cauchy deformation tensor (Astarita and Marrucci, 1974). The physical significance of $\mathbf{C}$ is that

$$|d\mathbf{X}|^2 = d\mathbf{r} \cdot \mathbf{C} \cdot d\mathbf{r}$$

Another surface deformation tensor $\mathrm{inv}_s\,\mathbf{C}$ or the surface inverse of $\mathbf{C}$ can be defined by

$$\mathrm{inv}_s\,\mathbf{C} \cdot \mathbf{C} = \mathbf{C} \cdot \mathrm{inv}_s\,\mathbf{C} = \mathbf{1}_s$$

$\mathrm{inv}_s\,\mathbf{C}$ is not to be confused with the conventional inverse of $\mathbf{C}$, $\mathbf{C}^{-1}$, which does not exist. Furthermore, $\mathrm{inv}_s\,\mathbf{C}$ is not the surface analogue of the Piola deformational tensor (Astarita and Marrucci, 1974) despite its definition. Such an analogue does not exist. Two surface strain tensors can now be defined by

$$\mathbf{G} = \mathbf{C} - \mathbf{1}_s$$

and

$$\mathbf{H} = \mathrm{inv}_s\,\mathbf{C} - \mathbf{1}_s$$

$\mathbf{G}$ is the surface analog of the Cauchy strain tensor (Astarita and Marrucci, 1974). However, $\mathbf{H}$ is not the surface analogue of the Finger strain tensor (Astarita and Marrucci, 1974) since, again, such an analogue does not exist because two-dimensional spaces do not have a volume. The surface strain tensor $\mathbf{L}$ appearing in the model is defined by

$$\mathbf{L} = 1/2(\mathbf{G} - \mathbf{H})$$

Finally, the scalar ψ appearing in the model is given by

$$\psi = 1/2(tr\,\mathbf{G} + tr\,\mathbf{H})$$

For the behavior of the above kinematical quantities in different surface flows, see Gardner (1975).

Manuscript received June 13, 1977; revision received December 5, and accepted December 16, 1977.

SCP Production on C_1 Compounds

Given the partial oxidation products of methane as the chemical feedstock for single-cell protein (SCP) production, their conversion efficiency is optimized by optimal selection of the pertinent microorganisms that can utilize the feedstock. The coenzymes of the three oxidation steps from methanol to formaldehyde to formate and carbon dioxide as well as the pathway involved in carbon fixation determine the cell-mass yield. Microorganisms which follows the ribulose monophosphate cycle and which have coenzymes which are linked to the maximum production of ATP (for example, NAD linked dehydrogenases), should be searched for economical production of SCP. Batch growth rate and yield data are limited in utilization and interpretation, and care should be exercised in their use. The subject of this case study, *Methylomonas* EP-1, gives an optimal cell mass yield of 65% and a stable chemostat operation at space velocities as high as 0.58 hr^{-1}.

ELEFTHERIOS PAPOUTSAKIS
HENRY C. LIM
and
GEORGE T. TSAO
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

SCOPE

Great interest has been expressed in the last decade in the production of single-cell protein (SCP) from C_1 compounds as a sole carbon and energy source. Although a few processes are currently on stream, several university and industrial research groups are highly involved in the development of various alternative SCP processes. In all these new ventures, multidisciplinary teams are cooperating at various project stages from fundamental,

---

Correspondence concerning this paper should be addressed to Henry C. Lim.

0001-1541-78-1019-0406-$01.45.