

The Apparent Dilational Viscoelastic Properties of Fluid Interfaces

IV. Determination of Surface Compositional Elasticity and Sorption Parameters

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Previous experimental data concerning the dilational rheological properties of fluid interfaces in longitudinal wave surface viscometers are reexamined in order to obtain new values of the compositional surface elasticity of surfactant solutions. Values of the elasticity as well as other equation of state parameters determined from these dynamic measurements are compared with thermodynamic values. The results are encouraging. The present analysis considers the effect of the surfactant adsorption-desorption rate processes in longitudinal wave experiments. The present analysis may be considered as an extension of the earlier work of Lucassen and van den Tempel and more recent work of Goodrich to monolayers, both of which are limited to diffusion-controlled cases.

INTRODUCTION

When surfactants adsorb at fluid-fluid interfaces, they create a surface phase that has both elastic and viscous properties. The elastic properties actually result from the surfactant mass transfer process that occurs when the surface is dilated or compressed. The knowledge of the interfacial dilational properties is important for the understanding and treatment of phenomena occurring at fluid interfaces in many multiphase operations, such as in foam and emulsion systems and in oil displacement that occurs during enhanced oil recovery by chemical flooding processes (1, 2).

A number of experimental techniques have been used to measure the dilational properties of fluid interfaces (3-10). One of the most promising methods involves the use of longitudinal waves developed by

Lucassen and van den Tempel and their collaborators (11-15), Maru, Djabbarah, and Wasan (16-18), Goodrich (19), and Panaiotov *et al.* (20). Determination of surface dilational properties involves measurement of the response of the surface subjected to dilational or compressional strains. These, in turn, are accompanied by mass transfer processes within the surface and, between the surface and the bulk.

Lucassen and van den Tempel analyzed the mass transfer process in dilute surfactant solutions involving the diffusional exchange of solute between bulk and surface (13). Their analysis is applicable to a case in which there is no adsorption or desorption barrier—that is, equilibrium is assumed between the surface and the subsurface. Furthermore, these investigators ignored the “intrinsic” rheological properties.

The present work treats the case of dilational displacements, in which the effects of mass transfer act in conjunction with intrinsic rheological properties. The role of

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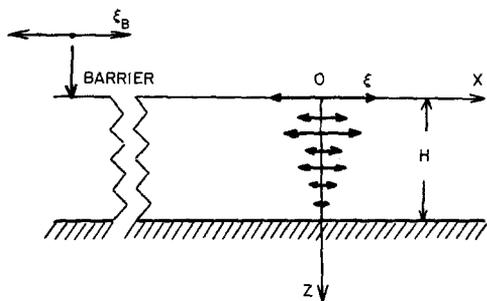


FIG. 1. Schematic of longitudinal wave motion on the surface.

mass transfer exchange is clarified, and the longitudinal wave technique is established as a method for generating data which can be used to estimate surfactant adsorption-desorption kinetics at fluid interfaces. Previous experimental data concerning the longitudinal wave technique of Lucassen, van den Tempel, and their collaborators are re-examined. Values of the compositional or Gibbs elasticity, E_0 , and $dC/d\Gamma$, as determined from the dynamic measurements are compared with thermodynamic values.

THEORETICAL ANALYSIS

1. The Response of a Bulk Fluid to Longitudinal Wave Motion at the Surface

We take the surface to be at rest at $z = 0$ as shown in Fig. 1. A sinusoidal wave propagates in the x direction in an infinitely long trough containing a viscous incompressible fluid. A movable barrier located at the surface of the fluid in the trough generates small-amplitude oscillations of frequency ω and wavelength λ . The wavelength is much larger than the characteristic length $(\nu/\omega)^{1/2}$, where ν is the kinematic viscosity of the fluid. The longitudinal wave will be damped in space and in time because of the irreversible processes taking place within the interface and the viscous dissipation within the bulk substrate. Under the longitudinal wave approximations (i.e., $|V_z| \ll |V_x|$ at $z = 0$), only the x component of

velocity needs to be considered (21). For small-amplitude waves, the linearized Navier-Stokes equations reduce to

$$\frac{\partial V_x}{\partial t} = \nu \frac{\partial^2 V_x}{\partial x^2} \quad [1.1]$$

With the same order of approximation, $\lambda \gg (\nu/\omega)^{1/2}$, the surface is considered to be flat, and the nonslip boundary condition at the surface becomes

$$V_x = V^s \quad \text{at } z = 0, \quad [1.2]$$

where V^s is the surface velocity.

The second boundary condition is applied at the bottom of the trough:

$$V_x = 0 \quad \text{at } z = H. \quad [1.3]$$

The solution for the wave motion of Eqs. [1.1], [1.2], and [1.3] is given by

$$V_x = \frac{\sinh(H-z)m}{\sinh mH} V^s, \quad [1.4]$$

where $V^s = V \exp(i\omega t + i\kappa x)$ and $m = (i\omega/\nu)^{1/2}$, since the wavenumber $\kappa \ll m$. From Eq. [1.4], the drag force exerted by the bulk upon the surface is

$$\rho\nu \left. \frac{\partial V_x}{\partial z} \right|_{z=0} = -\rho i\omega\nu \coth(mH) V^s. \quad [1.5]$$

2. Mass Transfer between the Surface and the Bulk Phase

Since all variables depend less on x than on z , the diffusion equation for the surfactant becomes

$$\frac{\partial \bar{C}}{\partial t} = D \frac{\partial^2 \bar{C}}{\partial z^2}, \quad [2.1]$$

where $\bar{C} = C - C_0$. Here, C_0 is the equilibrium concentration.

The mass flux of surfactant toward the surface can be expressed as

$$-D \left. \frac{\partial \bar{C}}{\partial z} \right|_{z=0} = \phi, \quad [2.2]$$

where

$$\phi = \phi(C, \Gamma). \quad [2.3]$$

We assume here that the mass flux, ϕ , of surfactant to the phase interface is a function of both the bulk concentration, C , in the adjacent bulk sublayer and the surface concentration, Γ . Therefore, we do not assume that equilibrium is achieved instantaneously between the interface and the bulk fluid at the interface. Hence our analysis allows for the adsorption-desorption barrier at the phase interface. Previous analysis of Lucassen and van den Tempel (13, 14) was restricted to the equilibrium assumption, and therefore it did not take into account the adsorption-desorption mechanism.

Under the assumptions already stated above concerning the slow variation of the surface velocity, V^s with x , and the dilation of the surface having a small amplitude, the departure of Γ and C from their equilibrium values caused by dilation will also be small. Then Eq. [2.3] can be linearized as follows.

Expanding the right-hand side of Eq. [2.3] in a Taylor series about $C = C_0$ and $\Gamma = \Gamma_0$, we have

$$\phi = k_1 \bar{C} - k_{-1} \bar{\Gamma}, \quad [2.4]$$

where

$$\bar{\Gamma} = \Gamma - \Gamma_0,$$

$$k_1 \equiv \left(\frac{\partial \phi}{\partial C} \right) \Big|_{\substack{C=C_0 \\ \Gamma=\Gamma_0}}$$

and

$$k_{-1} \equiv - \left(\frac{\partial \phi}{\partial \Gamma} \right) \Big|_{\substack{C=C_0 \\ \Gamma=\Gamma_0}} \quad [2.5]$$

since for an equilibrium process, there is no mass exchange between the surface and the bulk,

$$\phi(C_0, \Gamma_0) = 0.$$

The flux of surfactant toward the surface becomes

$$-D \frac{\partial \bar{C}}{\partial z} \Big|_{z=0} = k_1 \bar{C} - k_{-1} \bar{\Gamma} \quad \text{at } z = 0. \quad [2.6]$$

At the bottom of the trough,

$$\frac{\partial \bar{C}}{\partial z} = 0 \quad \text{at } z = H. \quad [2.7]$$

Equations [2.6] and [2.7] are the boundary conditions for the bulk diffusion Eq. [2.1]. The complete solution is

$$\bar{C} = \frac{k_{-1}[1 + \exp(-2nH)]\bar{\Gamma}}{nD[1 - \exp(-2nH)] + k_1[1 + \exp(-2nH)]}, \quad [2.8]$$

where $\bar{\Gamma} = G \exp(i\omega t + i\kappa x)$ and $n^2 = i\omega/D$.

Since the diffusivity of a surfactant is small, n is, in general, very large, as long as ω is not small (i.e., $\omega > 10^{-2}$ rad/sec). The depth of the layer of liquid in the trough is of the order of 1 cm. Then one can neglect the influence of the depth, and Eq. [2.8] becomes

$$\bar{C} = \frac{\bar{\Gamma}k_{-1}}{(i\omega D)^{1/2} + k_1}. \quad [2.9]$$

The net rate of mass transfer determined from Eqs. [2.4] and [2.9] is

$$\phi = -\bar{\Gamma}k_{-1} \frac{(i\omega D)^{1/2}}{(i\omega D)^{1/2} + k_1}. \quad [2.10]$$

Thus, the mass transfer flux from the bulk has been expressed only in terms of the surface concentration $\bar{\Gamma}$ and the physical constants.

3. Governing Equations for Surface Motion: Dispersion Equation

The linearized surface mass balance equation can be written as

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial(\Gamma V^s)}{\partial x} = -D \frac{\partial C}{\partial z} + D_s \frac{\partial^2 \Gamma}{\partial x^2}.$$

The surface diffusion term in the equation above can be neglected compared to the

other terms. Using the assumption that $\bar{\Gamma} \ll \Gamma_0$ and Eq. [2.10] for ϕ , the surface continuity equation can be written as

$$\frac{\partial \bar{\Gamma}}{\partial t} + \Gamma_0 \frac{\partial V^s}{\partial x} = \phi$$

$$= -\bar{\Gamma} k_{-1} \frac{(i\omega D)^{1/2}}{(i\omega D)^{1/2} + k_1} \quad [3.1]$$

The surface momentum balance equation is

$$\frac{\partial T_{xx}}{\partial x} + \rho\nu \left. \frac{\partial V_x}{\partial z} \right|_{z=0} = 0, \quad [3.2]$$

in which T_{xx} is the x component of the surface stress tensor. Equation [3.2] represents a relationship which expresses the mechanical coupling of the interface to the bulk substrate, and, involves the horizontal velocity component only, because we emphasize the longitudinal wave in this work. The second term on the left-hand side of this equation represents the drag which is given by Eq. [1.5].

We now propose to use Maxwell's model for a viscoelastic surface. After omitting the convective terms, the constitutive equation for T_{xx} becomes

$$(T_{xx} - \sigma) + t_m \frac{(T_{xx} - \sigma)}{\partial t} = \eta \frac{\partial V^s}{\partial x}, \quad [3.3]$$

where t_m is the Maxwell relaxation time, and η is the sum of intrinsic surface dilational and shear viscosity.

We now need information about the surface tension, σ , as a function of surface concentration, Γ .

The surface equation of state is

$$\sigma = \sigma(\Gamma). \quad [3.4]$$

After linearizing, Eq. [3.4] becomes

$$\sigma = \sigma - \sigma_0 = (\Gamma - \Gamma_0) \left. \frac{d\sigma}{d\Gamma} \right|_{\Gamma=\Gamma_0}$$

$$= -\frac{E_0}{\Gamma_0} \bar{\Gamma}, \quad [3.5]$$

where $E_0 = -\Gamma_0(d\sigma/d\Gamma)|_{\Gamma=\Gamma_0}$ is the Gibbs or

compositional elasticity. The wave solution of [3.1] to [3.5] is of the form

$$\bar{\Gamma} = G \exp i(\omega t + \kappa x),$$

$$V^s = V \exp i(\omega t + \kappa x),$$

$$T_{xx} - \sigma = T \exp i(\omega t + \kappa x). \quad [3.6]$$

Substituting Eq. [3.6] into Eqs. [3.1], [3.2], [3.3], [3.4], and [3.5], we obtain three algebraic equations in three unknowns:

$$(i\omega + \alpha)G + i\kappa\Gamma_0 V = 0,$$

$$i\kappa T - dV = 0,$$

$$(1 + i\omega t_m)T$$

$$+ \frac{E_0}{\Gamma_0} (1 + i\omega t_m)G - i\kappa\eta V = 0, \quad [3.7]$$

where

$$\alpha \equiv k_{-1} \frac{(i\omega D)^{1/2}}{(i\omega D)^{1/2} + k_1}$$

and

$$d = \rho(i\omega\nu)^{1/2} \coth\left(H\left(\frac{i\omega}{\nu}\right)^{1/2}\right).$$

Here G, V, T are the unknown constants. To ensure the existence of a nontrivial solution of the above system of linear algebraic equations, the determinant of the coefficients must be zero, i.e.,

$$\begin{vmatrix} i\kappa\Gamma_0 & i\omega + \alpha & 0 \\ -d & 0 & i\kappa \\ -i\kappa\eta & (E_0/\Gamma_0)(1 + i\omega t_m) & 1 + i\omega t_m \end{vmatrix} = 0$$

or

$$\kappa^2 = \frac{-d(i\omega + \alpha)(1 + i\omega t_m)}{(1 + i\omega t_m)E_0 + \eta(i\omega + \alpha)}. \quad [3.8]$$

Equation [3.8] is the dispersion equation relating the wavenumber κ to the surface and bulk properties. Here, d can be considered as the contribution of the bulk phase viscous drag upon the interface, and α as the adsorption-desorption rate.

In the limiting case of infinite depth, $d = \rho(i\omega\nu)^{1/2}$, and if there is no mass transfer interaction, then $\alpha = 0$. Neglecting the in-

trinsic properties and t_m , Eq. [3.8] can be simplified in the form

$$\kappa^2 = - \frac{\rho \omega i (i \omega \nu)^{1/2}}{\epsilon}, \quad [3.9]$$

where ϵ is the complex dilational modulus given by Eq. [5.3]. Equation [3.9] is the simplified equation first obtained by Lucasen (11). This equation shows that $\kappa \sim \omega^{3/4}$, which is a characteristic of insoluble monolayers.

PARAMETRIC STUDY

Because we are interested in aqueous surfactant solutions, the following values for the parameters in the dispersion equation are chosen:

$$\nu = 0.01 \text{ cm}^2/\text{sec},$$

$$\rho = 1 \text{ g/cm}^3,$$

$$H = 0.3-1.0 \text{ cm},$$

$$E_0 = 50 \text{ dyne/cm},$$

$$k_1 = 3.0 \times 10^{-4} - 1 \text{ cm/sec},$$

$$k_{-1} = 0.3-100 \text{ sec}^{-1},$$

$$\omega = 10^{-3}-10^3 \text{ rad/sec},$$

$$D = 10^{-5} \text{ cm}^2/\text{sec}.$$

The maximum value for the surface viscosity is chosen to be 3 surface poise. Maxwell relaxation time characterizes the memory of the surface. For monolayers of soluble surfactants without the formation of film aggregates, t_m is essentially a small value, i.e., the memory of the surface is short. Therefore, a reasonable value for the upper limit of t_m is 10^{-2} sec. To investigate the influence of these two parameters, t_m and η , the mass transfer is temporarily neglected in Eq. [3.8], and the expression can be written as

$$\kappa^2 = - \frac{i \omega d}{E_0 + i \omega \eta / (i \omega t_m + 1)} = - \frac{i \omega d}{E_0 + [\omega^2 t_m^2 / (1 + \omega^2 t_m^2)] (\eta / t_m) + i \omega \eta / (1 + \omega^2 t_m^2)} \quad [4.1]$$

As t_m/η approaches 1, the above equation shows that an increase of t_m strengthens the elastic effects and reduces the viscous effects; as t_m/η approaches infinity, the behavior of the surface is that of an ideal two-dimensional fluid without any intrinsic rheological properties.

Figure 2 displays plots of the real part of the wavenumber against frequency on a log-log chart. Figure 2a corresponds to the case when $t_m = 0$. It is noted that as the intrinsic surface viscosity, η , increases, the wavenumber decreases; while in Figs. 2b, c, and d, we observe that as the relaxation time increases, the wavenumber increases for a fixed value of η . The most important feature of these plots is that the wavenumber for $\eta \leq 0.03$, appears to be almost independent of t_m , with t_m varying between 0 and 0.03 sec. In fact, the lower the frequency, the less dependent the wavenumber is on both t_m and η . Therefore, for the case where $E_0 \geq 1$, $t_m \leq 10^{-2}$ and $\eta \leq 10^{-2}$, we can

neglect any intrinsic properties provided $\omega \leq 10$ rad/sec.

Using $t_m = 0$ and $\eta = 0$, Eq. [3.8] reduces

$$\kappa^2 = \frac{1}{E_0} \left(i \omega + \frac{k_{-1} (i \omega D)^{1/2}}{(i \omega D)^{1/2} + k_1} \right) \times \rho (i \omega \nu)^{1/2} \cdot \coth \left(H \left(\frac{i \omega \rho}{\nu} \right)^{1/2} \right). \quad [4.2]$$

The influence of the depth of the trough can now be calculated using Eq. [4.2]. It is noted from Fig. 3 that when the frequency is reduced to 10^{-2} rad/sec, the effect of finite depth is much greater than the effect of physical parameters describing the mass transfer processes. We can therefore conclude that in order to avoid the complication of intrinsic rheological properties, a frequency of no greater than 10 rad/sec must be used, and to eliminate the effect of finite depth, a frequency of no less than 10^{-2} rad/

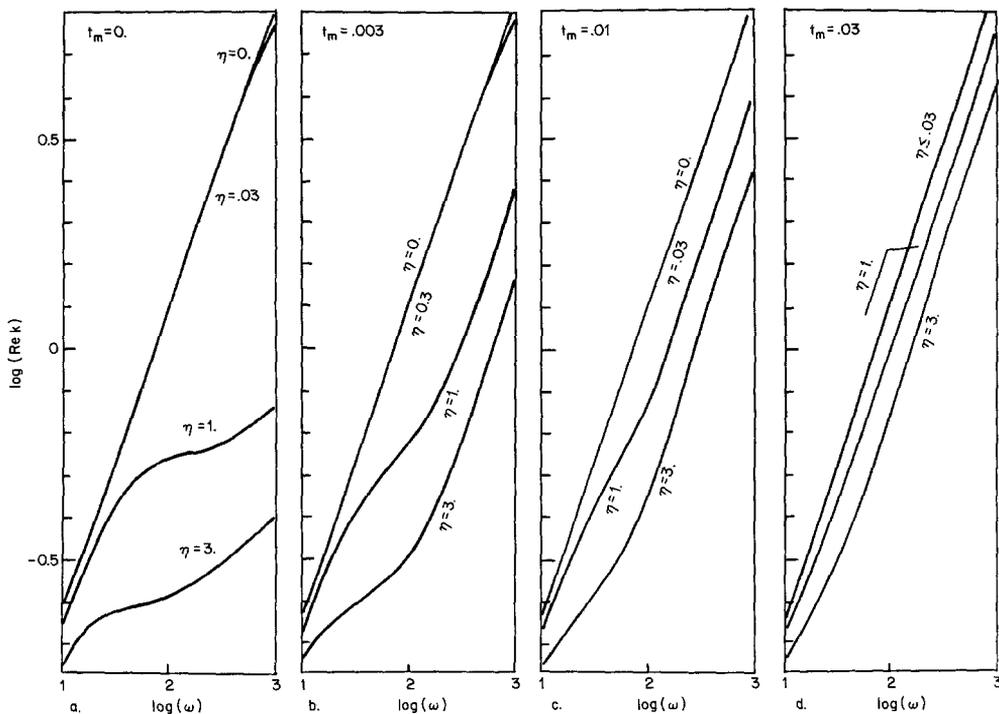


FIG. 2. The effect of viscoelastic properties on the wavenumber, κ .

sec must be used. Within this frequency range, the important parameters are Gibbs elasticity, E_0 , and the mass transfer rate constants, k_1 and k_{-1} .

The parametric study (see Fig. 4) shows the separate effect of k_1 and k_{-1} on wavenumber κ . We see that as k_1 increases, the influence of k_{-1} declines. Physically, a large k_1 is indicative of diffusion-control mass transfer at the surface; in such a case, only the ratio k_{-1}/k_1 is important. We note from Eq. [4.1] that when $k_1 \gg (i\omega D)^{1/2}$, α approaches k_{-1}/k_1 . Using the definition of k_{-1} and k_1 from Eq. [2.4], we find that for $k_1 \gg (i\omega D)^{1/2}$,

$$\frac{k_{-1}}{k_1} = \frac{dC}{d\Gamma}$$

The curves depicted in Fig. 4a for $k_1 = 0.1$ correspond to a diffusion controlled process since $(i\omega D)^{1/2} \ll 10^{-1}$. As we decrease the value of k_{-1} or the ratio k_{-1}/k_1 , the curves approach a limiting asymptote with a slope

of $3/4$ which is characteristic of insoluble monolayers as discussed above. Figures 4b, c, and d show the similar effects of adsorption-desorption rate on the wavenumber. Once again, as we decrease the value of k_{-1} , the surface approaches the insoluble monolayer behavior. The role of the adsorption-desorption rate process becomes more pronounced as k_1 decreases as is evident from the plots in Figs. 4a-d. For a fixed value of k_{-1} , if we decrease k_1 , the surfactant solubility appears to increase, and the Marangoni effect caused by the surface tension gradient is also reduced. Therefore, the surface loses its ability to transport waves, and we obtain a small value for the wavelength or a large value for the wavenumber as shown in Fig. 4.

DATA ANALYSIS AND PARAMETER ESTIMATION

Based on the conclusion of the parametric study discussed in the previous section, we

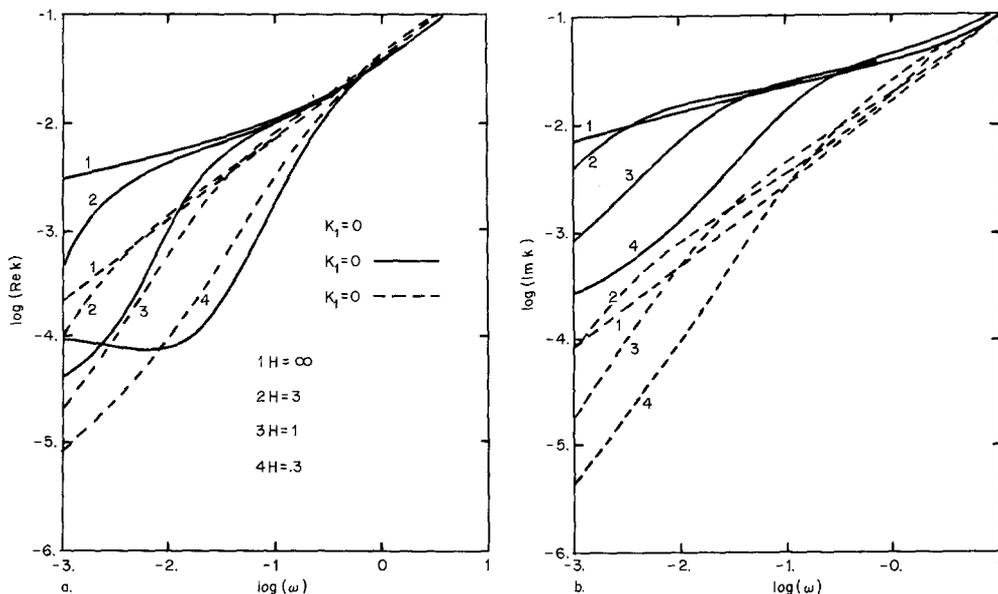


FIG. 3. The effect of trough depth on wavenumber (3a) and damping coefficient (3b).

can neglect the intrinsic rheological properties and obtain a simplified dispersion equation:

$$\kappa^2 E_0 + d(\alpha + i\omega) = 0. \quad [5.1]$$

The three unknown parameters $E_0, k_1,$ and k_{-1} can be calculated from the above relation if the wavenumber and frequency are known. Since Eq. [5.1] is a complex equation, more than two frequencies must be used for experimental data. The following equation was used to minimize the error between the experimental and the estimated values of E_0, k_1 and k_{-1} :

$$\min \left\{ \left[\sum_{j=1}^N \kappa_j^2 E_0 + d_j \frac{k_{-1}(i\omega_j D)^{1/2}}{(i\omega_j D)^{1/2} + k_1} + i\omega_j \right]^2 \right\}. \quad [5.2]$$

The method of "gold section" (22) was used here. For its application, however, one needs to know the interval of k_1 , where the minimum exists. The interval of k_1 was selected to be between 0 and 1.

Lucassen and van den Tempel (12) have reported values of the wavenumber κ and

damping coefficient ($\text{Im } \kappa$) as a function of frequency on the surface of the acidified solutions of decanoic acid for two bulk concentrations, namely, $C = 4.5 \times 10^{-8}$ and 10×10^{-8} mole/cm³. The frequency range covered in their experiments varied from 3.8 to about 25 rad/sec. Using these data and Eq. [5.2], we found the best fitted values of $\kappa, E_0, k_1,$ and k_{-1} . Our values of $E_0, k_1,$ and k_{-1} are tabulated in Tables I and II. Figure 5 displays the sample experimental data for κ of Lucassen and van den Tempel for $C = 10 \times 10^{-8}$ mole/cm³ and the solid lines are the results of our best fit to these data. In their experiments, the waves were generated by an oscillating barrier in a Langmuir trough and wave properties were obtained from surface tension changes at various distances from the barrier. The authors used these results to calculate surface dilational parameters by the following equation:

$$\epsilon = \frac{\rho\nu\omega m}{i\kappa^2} = \epsilon_{\text{app}} + i\omega\eta_{\text{app}}. \quad [5.3]$$

Here ϵ is the complex surface dilational modulus and ϵ_{app} and η_{app} are the apparent

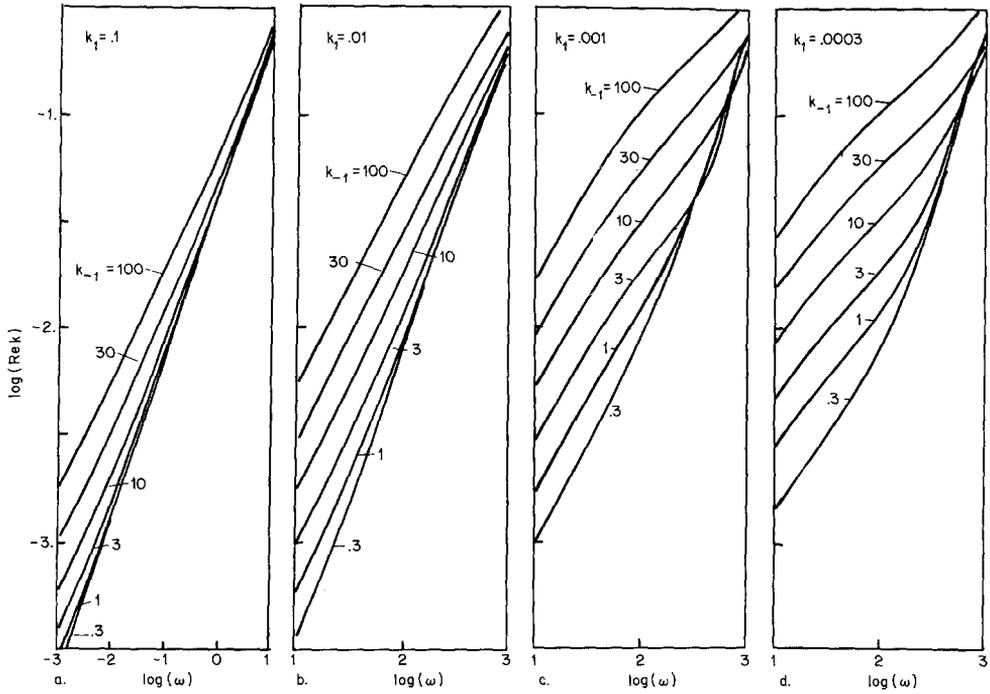


FIG. 4. The effect of sorption parameters on the wavenumber, κ .

surface dilational elasticity and viscosity parameters.

In their succeeding work, Lucassen and Van den Tempel (13) used low-frequency waves, i.e., long wavelength. Because of the finite length of the trough (8×60 cm), the reflected waves from the walls of the trough had to be considered by these investigators. They defined the dilational modulus as

$$\epsilon = \frac{d\sigma}{d \ln A} = \frac{\Delta\sigma}{(1/A)\Delta A}, \quad [5.4]$$

where A is the area of the surface element. The corresponding relative change in the area of a surface element is

$$\frac{\Delta A}{A} = \frac{\partial \xi}{\partial x}, \quad [5.5]$$

where ξ is the local displacement of the sur-

TABLE I

Comparison of Apparent and Surface Compositional Elasticity for Acidified Decanoic Acid Solutions

Concentration (mole/cm ³)	Frequency								Present work compositional surface elasticity, E_0 (dyne/cm)
	$\omega = 0.01$ rad/sec		$\omega = 0.1$ rad/sec		$\omega = 3.77$ rad/sec		$\omega = 25.3$ rad/sec		
	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)	
2.0×10^{-8}	2.8	2.2	7.0	3.9					14.5
3.0×10^{-8}	8.5	3.2	11.2	7.3					17.8
4.5×10^{-8}					35.5	10.5	46.1	6.1	52.0
10.0×10^{-8}					44.1	14.7	59.7	8.9	67.4

TABLE II
Sorption Parameters for Acidified Decanoic Acid Solutions

Concentration (mole/cm ³)	k_1 (cm/sec)	k_{-1} (l/sec)	Present work $\frac{dC}{d\Gamma} = \frac{k_{-1}}{k_1}$ (l/cm)	Thermodynamic values Maru and Wasan (17) $dC/d\Gamma$ (l/cm)
2.0×10^{-8}	9.1×10^{-4}	8.9×10^{-2}	97.9	152.1
3.0×10^{-8}	8.1×10^{-4}	9.9×10^{-2}	122.4	251.3
4.5×10^{-8}	4.0×10^{-2}	2.0×10	507.0	441.2
10.0×10^{-8}	2.7×10^{-2}	1.6×10	591.7	1397.0

face. By definition, the surface velocity V^s is given as

$$V^s = \frac{\partial \xi}{\partial t} = V e^{i(\kappa x + \omega t)} \quad [5.6]$$

Hence, we have

$$\xi = \frac{V}{i\omega} e^{i(\kappa x + \omega t)} \quad [5.7]$$

From Eqs. [5.5] and [5.7],

$$\frac{\Delta A}{A} = \frac{\partial \xi}{\partial x} = \frac{k}{\omega} V e^{i(\kappa x + \omega t)} \quad [5.8]$$

The equation of state, Eq. [3.5], gives

$$\Delta\sigma = \sigma - \sigma_0 = -\frac{E_0}{\Gamma_0} (\Gamma - \Gamma_0)$$

or

$$\Delta\sigma = -\frac{E_0}{\Gamma_0} G e^{i(\kappa x + \omega t)} \quad [5.9]$$

We have from Eq. [3.7]

$$G = -\frac{i\kappa\Gamma_0}{i\omega + \alpha} \quad [5.10]$$

From Eqs. [5.4], [5.8], [5.9], and [5.10], we obtain

$$\epsilon = \frac{i\omega E_0}{\alpha + i\omega} \quad [5.11]$$

or

$$\frac{i\omega}{\epsilon} E_0 - \left(\frac{k_{-1}(i\omega D)^{1/2}}{k_1 + (i\omega D)^{1/2}} + i\omega \right) = 0 \quad [5.12]$$

Lucassen and van den Tempel reported ϵ as a function of frequency for dilute solu-

tions of decanoic acid at bulk concentrations of $C = 2 \times 10^{-8}$ and 3×10^{-8} mole/cm³. These data were used in conjunction with Eq. [5.12] to estimate values of E_0 , k_1 , and k_{-1} . Our results for E_0 are tabulated in Table I. An examination of Table I, which shows only two extreme frequencies, reveals that as the frequency increases, the apparent elasticity, ϵ_{app} increases and tends to approach the true surface compositional or Gibbs elasticity, E_0 . These results also confirm the results of our parametric study, which indicates that at low frequency the contribution from the intrinsic elasticity is

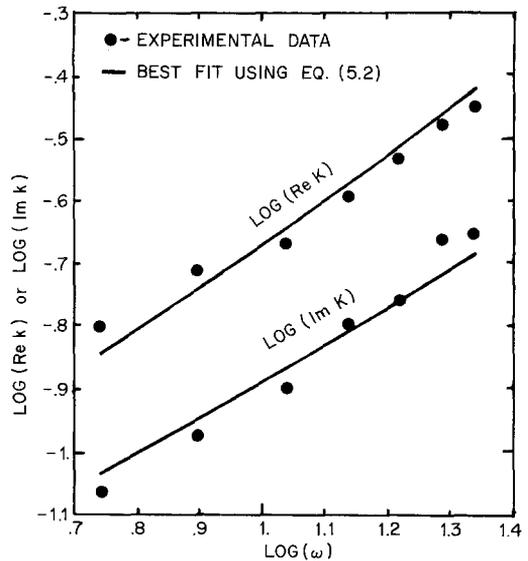


FIG. 5. Best fit to the longitudinal wave surface dilational data for the acidified decanoic acid solutions, $C = 10 \times 10^{-8}$ mole/cm³.

TABLE III

Comparison of Present Surface Elasticity Values with Thermodynamic Values for the Acidified Decanoic Acid Solutions

Concentration (moles/cm ³)	Present work elasticity E_0 (dyne/cm)	Thermodynamic values Maru and Wasan (17) (dyne/cm)
2.0×10^{-8}	14.5	13.3
3.0×10^{-8}	17.8	19.9
4.5×10^{-8}	52.0	29.9
10.0×10^{-8}	67.4	66.5

negligible and that the surface elasticity is compositional.

The calculated values of the sorption parameters k_1 and k_{-1} and their ratios $k_{-1}/k_1 = dC/d\Gamma$ are tabulated in Table II. It is noted that the values of k_{-1} are much larger than k_1 , suggesting that the molecular diffusion from the bulk is the major contributor to apparent viscoelastic properties for the dilute decanoic acid solutions. These findings are consistent with the earlier observations of Lucassen and van den Tempel (13) and Maru and Wasan (17). Furthermore, when the present values for the equation of state parameter $dC/d\Gamma$ for decanoic acid solutions are compared with the thermodynamic values, it is found that the values obtained by the two different methods are similar.

Table III compares the calculated values of the compositional elasticity with the

thermodynamic values. The latter have been recently tabulated by Maru and Wasan (17). The agreement is considered to be satisfactory.

Lucassen and Giles (14) determined the complex surface dilational modulus ϵ as a function of frequency for dodecyl triethylene glycol system, a nonionic surfactant. Their data are presented in Table IV together with our calculated values of E_0 . This table also compares the values for E_0 , which Lucassen and Giles estimated by employing a diffusion control model. It is interesting to note that the values for the surface compositional elasticities obtained by two different analyses compare favorably with each other.

Table V tabulates the calculated values of the parameters k_1 , k_{-1} , and $dC/d\Gamma$. The values of $dC/d\Gamma$ which represent the inverse of slopes of the surface adsorption curves are of same order of magnitude. It should also be pointed out that as the frequency increases, the apparent elasticity tends to approach the true compositional elasticity (see Table IV). In addition, the apparent surface viscosity first increases with increasing concentration, reaches a maximum, and then decreases at a fixed frequency. While at a fixed concentration, the viscous effects are much smaller compared to the elastic effect as the frequency increases. The time for surfactant exchange between the surface and the bulk decreases as the frequency increases, and hence the

TABLE IV

Comparison of Apparent Surface Elasticity with Compositional Elasticity as a Function of Concentration for Dodecyl Triethylene Glycol

Concentration (mole/cm ³)	Frequency				Present work surface compositional elasticity E_0 (dyne/cm)	Lucassen and Giles (14) (dyne/cm)
	$\omega = 0.0628$ rad/sec		$\omega = 6.28$ rad/sec			
	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)	ϵ_{app} (dyne/cm)	$\omega\eta_{app}$ (dyne/cm)		
0.5×10^{-9}	20.3	2.1	20.3	0.1	20.5	20.0
2×10^{-9}	25.3	8.7	33.4	0.1	35.6	35.0
10×10^{-9}	11.9	10.0	43.6	15.9	53.6	62.5
20×10^{-9}	7.9	6.1	45.5	8.9	61.3	76.0

TABLE V
Sorption Parameter for Dodecyl Triethylene Glycol System

Concentration (mole/cm ³)	k_1 (cm/sec)	k_{-1} (l/sec)	Present work $\frac{dC}{d\Gamma} = \frac{k_{-1}}{k_1}$ (l/cm)	Lucassen and Giles (14) $\frac{dC}{d\Gamma}$ (l/cm)
0.5×10^{-9}	2.5×10^{-4}	2.5×10^{-3}	9.7	5.6
2×10^{-9}	1.0×10^{-3}	2.0×10^{-2}	20.2	17.4
10×10^{-9}	3.2×10^{-3}	2.9×10^{-1}	92.7	132.6
20×10^{-9}	6.8×10^{-3}	1.2	180.4	208.2

surface behaves like a purely elastic insoluble monolayer.

CONCLUSIONS

The conclusions of the present analysis are summarized as follows:

(i) For frequencies less than 10 rad/sec, the contribution of intrinsic viscoelasticity can be neglected, except in those cases where surface compositional elasticity, $E_0 \ll 1 \text{ g/sec}^2$.

(ii) In this frequency range the Gibbs elasticity, E_0 , the sorption parameters k_1 , and k_{-1} , and trough depth H remain the most important parameters.

(iii) The most informative range of frequencies for the determination of k_1 and k_{-1} is $\omega \geq 10^{-2}$ rad/sec, in which the influence of depth is negligible.

(iv) Dynamic experiments have been used to obtain values of the compositional surface elasticity, E_0 , which is, in fact, a thermodynamic property of surfactant solutions. Longitudinal wave surface dilational data yield values for E_0 which agree with the thermodynamic values.

(v) The equation of state parameter, such as $dC/d\Gamma$, determined from these dynamic measurements compare favorably with the thermodynamic values.

(vi) The effect of the surfactant adsorption-desorption rate processes in the longitudinal wave experiments may be estimated using the analysis proposed here.

APPENDIX: NOTATION

A	Surface element area
Arg	Argument of a complex number
C	Bulk concentration of surfactant
D	Bulk diffusivity of surfactant
d	Constant defined in [3.7]
E_0	Gibbs elasticity
Im	Imaginary part of a complex number
H	Depth of bulk fluid
G	Constant defined in [3.6]
κ	Complex wave number
k, k_{-1}	Constants defined in [2.4]
m	Complex constant, defined in [1.4]
n	Complex constant, defined in [2.8]
Re	Real part of a complex number
T_{xx}	Component of surface stress tensor
T	Constant defined in [3.6]
t_m	Maxwell relaxation time
V	Constant defined in [1.4]
V^s	Surface velocity
V_x	x Component of bulk velocity

Greek symbols

α	Constant defined in (3.7)
β	Damping coefficient
Γ	Surface excess concentration
ϵ	Complex dilational modulus
ϵ_{app}	Dilational elasticity defined in (5.3)
ν	Bulk phase kinematic viscosity
η_{app}	Dilational viscosity defined in (5.3)
θ	Phase lag
η	Intrinsic surface viscosity
λ	Wavelength
ξ	Local displacement of the surface

ρ	Bulk phase density
σ	Surface tension
ϕ	Mass flux
ω	Frequency

Subscripts

0	Equilibrium quantity
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