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INTERFACIAL VISCOELASTICITY IN EMULSIONS AND FOAMS

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Abstract

Both the generation and the stability of emulsions and foams depend on interfacial properties induced by adsorbed surfactants. The essential function of surfactants during emulsification and foaming is not that they reduce the equilibrium interfacial tension, but they impart specific dynamic properties to the interface. A surfactant-covered interface behaves as a two-dimensional body with its own elasticity and viscosity, which are related to the non-equilibrium values of the interfacial tension. Such viscoelasticity is a significant factor in any liquid flow near the interface, and in the stability of the thin films separating emulsion drops or foam bubbles. Numerically, values of the viscoelasticity vary over a wide range, depending on surfactant parameters, on rate of surface deformation and on any relaxation processes driving the interfacial tension to its equilibrium. A quantitative framework is available for the evaluation of these rheological parameters, and of the dynamic surface tension of surfactant solutions, if the relaxation mechanism is diffusional interchange between surface and solution. We review both theoretical and experimental information on the dynamic surface behaviour of surfactants, and indicate possible routes to a quantitative model for their functionality in food emulsions and foams.

Key Words: Emulsification, emulsifier, emulsion stability, dynamic surface properties, diffusional relaxation, Gibbs elasticity, surface dilational modulus, surface dilational elasticity, surface dilational viscosity.

Introduction

The very existence of emulsions and foams has long been known to depend on the presence of emulsifiers and foamers, i.e., surface active molecules which are adsorbed at the interface from the continuous liquid phase. The primary effect of such molecular adsorption is that it reduces the tension of the interface. However, reduction of the interfacial tension cannot in itself explain the formation of emulsions and foams with more than transient stability. If this were the case, it should be possible to prepare emulsions in the absence of surface active solutes, from pure low-tension liquids. In practice, it is impossible to obtain emulsions with any degree of stability in this way. The essential stabilising function of surface active molecules during emulsification is to enable the interface to resist tangential stresses from the adjoining flowing liquids (van den Tempel, 1960). An emulsifier-covered interface, therefore, can behave as a two-dimensional body with its own rheological properties. These provide the liquid films separating emulsion drops with a mechanism for dynamic stabilisation, without which any two drops just formed would be liable to immediate coalescence during the emulsification process.

The present paper reviews background and existing data on the rheology of interfaces and indicates how rheological parameters can be estimated in areas where measurements are difficult.

Relevance of Interfacial Rheology for Liquid Film Stability

The main mechanism by which a surfactant aids emulsification and foaming is that its presence can lead to gradients in interfacial tension, which enable the interface to resist tangential stresses. Figure 1 illustrates how such gradients can produce a resistance against local thinning of the liquid film separating two emulsion drops or foam bubbles, and so prevent coalescence. Without surfactant, such a liquid film has a uniform interfacial tension (σ), and is insufficiently stable against rupture induced by any sudden local disturbance of its surface. In the presence of surfactant, however, the
same disturbance will create a momentary gradient in adsorption and hence a gradient in interfacial tension. Interfaces can be likened to elastic membranes, in which regions of high tension tend to contract more strongly than do low-tension regions. Film areas with high interfacial tension, therefore, exert a pull on adjacent lower-tension areas, which results in a flow of surface adhering liquid towards the thin spot in the film. In this manner, surfactants added as emulsifiers or foaming agents can make a surface resist any deformation that would create a gradient surface tension, and so they provide the film with a self-healing mechanism. Moreover, a sufficiently rigid adsorption layer can slow down drainage of the liquid film to a considerable degree, and a sufficiently rigid adsorption layer can slow down drainage of the liquid film to a considerable degree, and thus contribute to the long-term stability of emulsions and foams.

Qualitatively, the effect of a surface's resistance against tension gradients has been described more than a century ago by Marangoni (1872) and Gibbs (1878). Quantitatively, the measurement of this resistance is from the last few decades, and so is the interpretation of the results in terms of surfactant properties.

**Definition of Interfacial Rheological Parameters**

Interfacial or two-dimensional rheology, like its more familiar three-dimensional counterpart, defines the functional relationship between stress, deformation and rate of deformation in terms of coefficients of elasticity and viscosity. In both two and three dimensions, different types of deformation of fluid elements are possible, with different elastic and viscous coefficients. Two main types are illustrated in Figure 2 for a two-dimensional system:

1. **Shear**, i.e., changes in shape at constant area or volume;
2. **Compression/dilation**, i.e., changes in area or volume at constant shape.

However, the analogy between 2-D and 3-D rheology is far from complete and can be misleading, as has been pointed out (van den Tempel, 1977). One major difference is that the interface is not an autonomous system: it exists only as a boundary between two bulk phases. Its motion is always coupled to that of the adjoining 3-D phases, and "intrinsic" surface properties cannot be separated from substrate effects without arbitrariness. Because of this non-autonomy, contents and composition of an interface can change during an experiment. This will be shown to result in unusual rheological behaviour, especially in emulsions and foams. Another important difference between two- and three-dimensional systems is that, in many instances of practical application, 3-D liquids can be considered incompressible, i.e., their molecular volume is constant. In the 2-D case, however, surfactant-covered interfaces do not have constant molecular areas: such interfaces can be compressed and expanded over a range of areas stretching in practice from 0.3 to more than 10 nm²/molecule. Accordingly, reported viscosities of 3-D liquids generally do not refer to compressional but to shearing deformation, but in 2-D systems "surface viscosity" must be specified as measured either in shear or in compression/dilation. Surface shear viscosity has traditionally enjoyed the greater popularity with experimentalists (Goodrich et al., 1975; Mohan et al., 1976), especially in food systems (Dickinson et al., 1988; Martinez-Mendoza and Sherman, 1990; Kiosseoglou, 1992). The quantitative determination of surface dilational elasticity and viscosity has come into focus during the last few decades (Lucassen and van den Tempel, 1972; Wasan et al., 1979). The emphasis in the present paper will be on these dilational properties.

In the case of compression/dilation, the surface stress, \( \Delta \sigma \), resulting from small area variations, \( \Delta A \), can be expressed as the sum of an elastic and a viscous contribution, with the latter depending on the relative rate of the area variation:

\[
\Delta \sigma = \epsilon_d \Delta \ln A + \eta_d \frac{d \ln A}{dt}
\]  \( \text{(1)} \)

The elastic coefficient \( \epsilon_d \) is a measure of the recoverable energy stored in the interface, while the viscous coefficient \( \eta_d \) reflects the loss of energy through relaxation processes, i.e., any spontaneous processes which affect the surface tension within the time scale of the experiment.

Contrary to what is often considered normal practice in shearing deformation, the elastic component cannot be ignored in compression/dilation. In fact, the elastic contribution to the surface stress generally predominates over that of viscosity in many emulsions and foams. The two coefficients \( \epsilon_d \) and \( \eta_d \) can be combined into a single modulus of viscoelasticity, \( \epsilon \), defined as the increase in surface tension for a unit of relative increase in surface area:

\[
\epsilon = \frac{d \sigma}{d \ln A}
\]  \( \text{(2)} \)

This definition, originally proposed by Gibbs for the surface elasticity of a soap-stabilised liquid film, has since been found to be of general applicability to express surface tension gradients on any liquid interface. The parameter \( \epsilon \) goes under the various names of "areal elasticity", or "compressional modulus" or, in the general case of both elastic and viscous behaviour, "surface dilational modulus". In the latter case, these two contributions can be measured separately by subjecting the interface to small periodic contractions and expansions at a given frequency. In such experiments the viscoelastic modulus \( \epsilon \) is a complex number, with a real part (the storage modulus) equal to the elasticity, \( \epsilon_d \), and the imaginary part (loss modulus) given by the product of the viscosity, \( \eta_d \), and the frequency (\( \omega \)) of the area...
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variations:

\[ \epsilon = \epsilon_0 + i \omega \eta \]  

(3)

which is equivalent to eq. 1. Experimentally, the imaginary contribution to the modulus \( \epsilon \) is reflected in a phase difference between stress (\( \Delta \sigma \)) and strain (\( \Delta A \)), as will be illustrated in Experimental Methods and Results.

Theoretical Evaluation of Dilational Elasticity and Viscosity

Surface tension changes due to area changes can be evaluated from independently measurable information in a number of cases. In simple cases the elasticity can be deduced from the "surface equation of state", i.e., from the equilibrium relationship between surface tension and adsorption, \( \Gamma \), of the surfactant. The immediate effect of a surface expansion, as illustrated in Figure 2, is a decrease in adsorption. If there is no re-supply of surfactant from the adjoining bulk solution (i.e., \( \Gamma \times A \) is constant), and if, moreover, the surface tension adjusts instantaneously to the equilibrium value for the new adsorption, we find a limiting value \( \epsilon_0 \) for the elasticity:

\[ \epsilon_0 = \left( \frac{-d\sigma}{d\ln \Gamma} \right)_{eq} \]

and a zero value for the viscosity. Deviations from this simple limit occur when relaxation processes in or near the surface affect either \( \sigma \) or \( \Gamma \) within the time of the measurement.

Examples of such relaxation processes during surface expansion are: (i) diffusion of surfactant to the surface from deeper layers of solution; and (ii) re-arrangement of adsorbed molecules within the surface.

The former process, in particular, is inevitable in emulsions and foams, where solubility is a necessary characteristic of the surface active material. The upshot of such a relaxation process generally is a lower elasticity than given by the limiting value \( \epsilon_0 \). The effect is easily evaluated for the case of the Gibbs elasticity of a thin liquid layer, bounded by two interfaces, which models the continuous phase separating foam bubbles or emulsion droplets.

Gibbs elasticity of thin films

After rapid expansion of a film element (thickness \( h \), surfactant concentration \( \sigma \)), illustrated in Figure 3, \( \epsilon_0 \) will be the initial value for the elasticity of each surface, i.e., before diffusion from the bulk of the liquid layer sets in. After diffusion has run its course, the final concentration and adsorption are slightly lower because the constant total amount of material is now distributed over a larger interfacial area and the same volume. Gibbs elasticity is defined in terms of the new surface tension at the end of this diffusional equilibration, and for films of such dimensions that diffusion

Figure 1. Result of surface disturbance in thin liquid layer separating two emulsion drops or foam bubbles. •: adsorbed surfactant molecule. Arrows: flow of surface and bulk liquid.

Figure 2. Resistance of surfactant-covered surface against deformation. Dotted area: undeformed surface element; bold lines: element after deformation.

Figure 3. Elastic resistance of thin film against area extension. Note that the change in adsorption (\( \Delta \Gamma \)) is negative for positive \( \Delta A \).
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This means that the surfactant-related quantities in eq. 5 depend on concentration according to:

$$e_0 = \frac{RT\Gamma^*}{a} \frac{c}{a} \quad ; \quad \frac{dc}{d\Gamma} = \frac{a}{\Gamma^*} \left(1 + \frac{c}{a}\right)^2$$

The final result for the elasticity of each film surface in Figure 3 is obtained by substitution into eq. 5:

$$E_s = \frac{RT\Gamma^*}{1 + (ab/2\Gamma^*)} \left(1 + \frac{c}{a}\right)^2$$

Gibbs elasticity always depends on surfactant concentration in the manner shown in Figure 4, at a given constant film thickness. In the low-concentration range, a linear increase of the elasticity is observed, followed by a maximum reached at a concentration \( c = a \) where the surface is approximately half saturated. At still higher concentrations, the elasticity falls off due to diffusion increasingly re-supplying the surface and levelling the initial gradient in interfacial tension. It must be emphasised that the characteristic maximum in the elasticity is not caused by any molecular interactions in the surface, but purely by the effect of increased diffusion from the solution at higher concentrations. Molecular interactions could not play a part in this case, anyway, because Langmuir adsorption presupposes ideal surface behaviour.

Apart from the surfactant’s concentration and its characteristic parameters, \( a \) and \( \Gamma^* \), the elasticity depends on the thickness of the film, because the film acts as a reservoir from which molecules can be re-supplied to the expanded surface: the elasticity of a thin film is always higher than of a thicker one, at the same concentration. For a very thin film from which no re-supply can take place at all, the limiting value equals \( e_0 \):

$$E_s = e_0 \quad \text{for} \quad h << \frac{2\Gamma}{dc} \quad (10)$$

Gibbs elasticity, as evaluated above, is regarded as a crucial parameter in stabilising thin films against rupture (Kitchener, 1962; van den Tempel et al., 1965; Prins et al., 1967; Malysa et al., 1991). It should be pointed out that its relation to film stability is nowhere near a simple proportionality. If it was, films would be best stabilised by insoluble surfactants, as these result in the highest film elasticities: see Figure 4 for \( a = 0 \). The effect of Gibbs elasticity is indirect: required for film stability is not so much that the Gibbs elasticity be high, but that it be higher in thin parts of the film than in its thicker parts (Gibbs, 1878; Lucassen, 1981). This condition is always fulfilled, according to eq. 5, if the concentration of the surfactant can be kept constant. However, in dynamic situations where the film surfaces are continuously expanded, the concentration is not constant: it decreases because of adsorption to the newly-created surface area. For such continuous surface expansion,
Gibbs’ requirement can only be fulfilled in the range where the Gibbs elasticity increases with decreasing concentration, i.e., at concentrations above that of the maximum in Figure 4.

Gibbs' elasticity of liquid films is a simplified example of surface rheological behaviour where diffusional re-supply is supposed to take place from a limited reservoir but is given unlimited time. The limited reservoir being the liquid film separating the emulsion drops means that Gibbs elasticity can be significant only if the emulsifier is present in the continuous phase. This provides a physical explanation for the well-known Bancroft rule, according to which emulsifiers should be soluble in what is to become the continuous phase rather than in the drop phase. These concepts will be generalised below by considering the surface dilational modulus measured over shorter time scales on thicker liquid layers.

Surface elasticity and viscosity

Elasticity and viscosity for thicker layers of surfactant solution have measurable values only if the interfacial area is expanded or compressed at a sufficiently fast rate. If the area changes are very slow, all surface tension gradients will be levelled out by (convective) diffusion to or from the underlying solution. Relaxation of the surface tension by diffusion is the most common relaxation mechanism in emulsions and foams, and is illustrated in Figure 5. It is governed by the characteristic time scale of the diffusion process, \( \tau_{\text{diff}} \), which can be defined by

\[
\tau_{\text{diff}} = \frac{2}{D} \left( \frac{d\Gamma}{dc} \right)^2
\]

where \( D \) is the surfactant's diffusion coefficient, and \( \frac{d\Gamma}{dc} \) measures the penetration depth of the diffusion. Obviously, diffusion can play no part at all in experiments performed in a time scale much smaller than \( \tau_{\text{diff}} \). In periodic compression/expansion with frequency \( \omega \), the time scale of the experiment can be equated to \( 1/\omega \), and the high-frequency limit for the modulus defined in eq. 3 is a pure elasticity:

\[
e_{d} = e_{0} ; \eta_{d} = 0 \quad \text{for } \omega \tau_{\text{diff}} \gg 1 \quad (12)
\]

The evaluation of elasticity and viscosity for slower area changes is more complex than that of Gibbs elasticity. For small-amplitude periodic compression/expansion the quantitative treatment in terms of diffusion following Fick’s laws results in:

\[
e_{d} = e_{0} \frac{1 + (\omega \tau_{\text{diff}})^{-1/2}}{1 + 2(\omega \tau_{\text{diff}})^{-1/2} + (\omega \tau_{\text{diff}})} \quad (13)
\]

\[
\omega \eta_{d} = \frac{(\omega \tau_{\text{diff}})^{1/2}}{1 + 2(\omega \tau_{\text{diff}})^{-1} + (\omega \tau_{\text{diff}})} \quad (14)
\]

for the elasticity and viscosity, respectively (Lucassen-Reynders and Lucassen, 1969). Several interesting features can be deduced from these expressions. First, surface behaviour for diffusional relaxation is always viscoelastic. It cannot be purely viscous, as the elastic contribution to the modulus \( \epsilon \) always remains larger than the viscous one. Second, for very slow deformations (i.e., at low \( \omega \)), where the two contributions \( \epsilon_{d} \) and \( \omega \eta_{d} \) tend to very low and almost equal values, the viscosity itself remains rate-dependent, and there is no range of Newtonian surface behaviour with constant viscosity (van den Tempel, 1977). The root of this unusual behaviour, which has no direct parallel in 3-D rheology, lies in the nature of diffusional relaxation, illustrated in Figure 5. This mechanism implies supply of material from outside the surface, and this supply is rate dependent: the surface elements under deformation do not have a constant composition and, therefore, cannot have rate-independent coefficients. Thus, the surface dilational viscosity given by eq. 14 is not, and cannot be, an "intrinsic" surface property because diffusional interchange with the adjoining solution is not intrinsic to the surface. For this reason, some authors refrain from using the term "surface viscosity" in this case; however, the operational definition of surface viscosity in eqs. 1-3 covers all relaxation mechanisms that change the surface tension, and this includes diffusional interchange with the solution.

Two other conclusions can be drawn from eqs. 13 and 14 by combining the elastic and viscous contributions in the absolute value, \( |\epsilon| \), of the complex modulus:

\[
|\epsilon|/e_{0} = \left[ 1 + 2(\omega \tau_{\text{diff}})^{-1/2} + (\omega \tau_{\text{diff}}) \right]^{-1/2} \quad (15)
\]

This implies that the frequency spectrum of the modulus, expressed in units \( e_{0} \), as a function of the dimensionless frequency, \( \omega \tau_{\text{diff}} \), is represented by a single curve for any surfactant at any concentration: the characteristics.
of individual surfactants are reflected in the numerical values of $\varepsilon_0$ and $\tau_{ad}$ but not in the shape of the curve. This curve is shown in Figure 6, and can be used as a master curve to identify diffusional relaxation. An important message of this modulus spectrum is that there is always a range of high frequencies where diffusional exchange with the adjoining bulk solution is negligible and eq. 12 becomes valid; here the adsorbed surfactant behaves as if insoluble even though it may be very soluble over longer time spans. The transition between "soluble" and "insoluble" can be suitably defined as indicated in Figure 6. For rates of surface deformation above this transition frequency, the modulus retains more than half of its limiting value $\varepsilon_0$, and the viscous contribution to it is small; for rates below the transition frequency, the modulus progressively decreases until vanishingly small at $\omega \tau_{diff} < < 1$. At such low rates of deformation, diffusion completely short-circuits all surface tension gradients: surface behaviour is that of a pure solvent without any adsorbed surfactant, although with a much lower tension than the really pure solvent.

A final interesting point concerns the concentration dependence of the modulus with its elastic and viscous parts. As in the case of the film elasticity, we need the "surface equation of state" of the monolayer for an analytical relationship in terms of surfactant concentration. Figure 7 illustrates the concentration dependence of the modulus, again for the simple case of Langmuir adsorption, eqs. 6-8, for a given frequency of area deformation. The resemblance with Figure 4 for the Gibbs elasticity for a given film thickness is striking and almost quantitative. The near-quantitative analogy between the two parameters was first noted by Lucassen and Hansen (1967): the limited time ($1/\omega$) available for diffusion during periodic area expansion/compression implies that diffusion can be effective only from/to a limited layer ($h/2$) of solution. The analogy is illustrated in Figure 8.

We may conclude that interfaces relaxing purely through diffusional exchange of molecules with a single-surfactant solution can be described quantitatively by eqs. 13-15. In addition, other relaxation mechanisms may also affect tension and viscoelastic behaviour of an interface depending on the time scale considered. Examples of relaxation processes that may occur in time scales ranging from $10^{-2}$ to $10^{+3}$ seconds are (van den Tempel and Lucassen-Reynders, 1983): (i) retardation of adsorption by an adsorption "barrier" (Bleys and Joos, 1985); (ii) slow re-orientation of molecules after adsorption; (iii) complex formation and phase transitions in the surface; and (iv) formation or destruction of 3-D structures. These can occur either in the surface as in collapsed monolayers (Veer and van den Tempel, 1972) or in the solution, e.g., micelles (Lucassen, 1975; Fang and Joos, 1992).

In most technological and biological applications, these relaxation phenomena occur in combination with diffusion. Theory for such "mixed" relaxation is fairly complex, and beyond the scope of this paper.

Figure 6. Modulus spectrum for diffusional relaxation. (- - ) limiting behaviour for fast and slow diffusion.

Figure 7. Numerical example of surface dilational modulus as a function of surfactant concentration ($c$), calculated from eq. 15 for Langmuir adsorption with $\text{RTT}^\infty = 20 \text{ mN/m}$; frequency $\omega = 400 \text{ s}^{-1}$; $D = 10^{-10} \text{ m}^2/\text{s}$. Half-saturation concentrations $a$ as in Figure 4.
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Surface expansion —— gradient in tension
affected by limited diffusion during/from

time: 1/ω  
depth: infinite

Figure 8. Analogy between surface modulus of bulk solution and Gibbs elasticity of thin film. Modulus measured at frequency ω means Gibbs elasticity measured at thickness h/2 = (D/ω)1/2.

Dynamic surface tension as a function of time

The surface dilational modulus c as defined in eq. 2 describes the dynamic surface tension resulting from a change in the surface area of a surfactant solution. Its value was found to depend on relaxation mechanisms driving the tension back to its equilibrium value. The same relaxation processes determine the dynamic surface tension of a freshly-created interface when the new area is kept constant. The kinetics of adsorption during the equilibration of such an interface has been described by diffusion theory (Ward and Tordai, 1946). In an important development, Loglio et al. (1991) have shown theoretically that the same functions which determine the frequency dependence of the modulus c can also be used to describe the time dependence of the dynamic surface tension at constant area. For instance, the dynamic surface tension near the end of the equilibration, i.e., at long equilibration time t, is known to vary according to t−1/2; this corresponds to the ω−1/2 dependence of the modulus at the low-frequency end of the spectrum in eq. 15. Thus, the surface tension versus time curve of an equilibrating surfactant solution can be translated into a modulus spectrum as given in Figure 6, and vice versa; measurements of either quantity can be used to obtain information on the other in time scales where direct measurements of the latter meet with experimental difficulties.

Experimental Methods and Results

Methods

Experimental techniques used for studying dilational viscoelasticity of surfaces roughly fall under two headings:
(i) methods involving small-amplitude periodic compression and expansion of a surface, including surface wave techniques (Lucassen and van den Tempel, 1972; Lucassen and Giles, 1975; Ting et al., 1985; Kokelaar et al., 1991) and oscillating bubbles (Lunkenheimer et al., 1984); and

(ii) methods subjecting the surface of a solution to a large continuous expansion (van Voorst Vader et al., 1964; Defay and Petre, 1971; Van Hunsel et al., 1989; Kao et al., 1992). In such experiments, if carried out at a constant relative rate of surface expansion (d ln A/dt), a steady state is reached eventually, with a constant value of Δσ. The area changes here are too large for eq. 1 to be valid, but the ratio between Δσ and d ln A/dt can be defined as an apparent surface dilatational viscosity (van Voorst Vader et al., 1964). It has been shown that this steady-state "viscosity" contains an elastic contribution and, in fact, corresponds closely to the value of c/ω given by eq. 15 for small-amplitude periodic experiments over a range of low frequencies (Lucassen and Giles, 1975).

Thus, essentially similar information can be extracted from experiments with these two types of methods. In view of this essential equivalence, a brief description of the former type will suffice.

In time scales roughly from 10−2 to 10−3 seconds, surfaces are conveniently compressed and expanded by sinusoidal motion of a barrier at a given frequency, ω. For smaller time scales, the technique of light scattering by surfaces in thermal motion has been reviewed by Langevin (1991). Strictly speaking, the deformation generated by barrier movement is not the isotropic area change illustrated in Figure 2; it also contains a shear component. Interference by shear effects is lessened by having two barriers oscillating in counter movement, as illustrated in Figure 9. In the simple case where the surface undergoes a uniform deformation, the fluctuations in surface tension monitored by a Wilhelmy plate can be related directly with the area fluctuations as shown in Figure 10. Any relaxation process occurring within the time scale of the experiment, i.e., within 1/ω s, will cause a time lag between the fluctuations in surface tension and those in the surface area. When these fluctuations are displayed on an X-Y recorder, such a time lag
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**Sinusoidal Area Compression/Expansion:**

\[ \Delta A = f(t) \]

\[ \text{Elastic Surface} \]

**Response of Surface Tension:**

\[ \Delta \sigma = f(t) \]

\[ \text{Viscoelastic Surface} \]

\[ \text{Elastic Surface} \]

**Figure 10.** Result of periodic area variation at constant frequency, for purely elastic and for viscoelastic behaviour (A). Display on XY recorder (B).

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**Table 1.** Dilational and shear properties of protein-covered surfaces. Experimental results for 0.03\% protein solutions, aged 2 hours, at relative rate of air/water surface deformation 0.084 s\(^{-1}\) (Benjamin and Van Voorst Vader, 1992).

<table>
<thead>
<tr>
<th>Protein</th>
<th>Dilational Modulus (mN/m)</th>
<th>Shear Modulus (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ovalbumin</td>
<td>57</td>
<td>0</td>
</tr>
<tr>
<td>Bovine Serum Albumin</td>
<td>46</td>
<td>10</td>
</tr>
<tr>
<td>Sodium Caseinate</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

turns the straight line found for purely elastic behaviour into a tilted ellipse from which both the elastic and the viscous contribution to the modulus can be evaluated. Experimental results are usually expressed as the absolute value of the modulus, \(|\epsilon|\), and the viscous loss angle which reflects the ratio between viscous and elastic contributions.

**Results**

Figure 11 presents a classical example of experimental modulus values obtained as a function of surfactant concentration at several constant frequencies (Lucassen and van den Tempel, 1972). The curves are seen to conform to the curves calculated for diffusion relaxation in Figure 7, and for each concentration the frequency dependence is in qualitative agreement with Figure 6. From the measured viscous loss angles (not reproduced here), the separate contributions of elasticity and viscosity can be evaluated; as an example, for the highest modulus measured (i.e., the maximum at the highest frequency) we find:

- surface dilational elasticity \(\epsilon_d = 25\) mN/m;
- surface dilational viscosity \(\eta_d = 12.5\) mPa s (\(= 12.5\) surface Poise).

At this concentration and frequency, surface behaviour is still mainly elastic, even though the numerical value of the viscosity is very high in comparison with the surface shear viscosity of similar molecules (see below). At higher concentrations and/or lower frequencies the diffusional relaxation progressively lowers the total modulus while the viscous contribution to it increases without ever exceeding the elastic contribution. The same picture of purely diffusional relaxation has been confirmed from measurements on a number of other pure surfactants, and also on mixtures (Garrett and Joos, 1976). Mixtures of surfactants have also been used to demonstrate the equivalence of the modulus spectrum and the dynamic surface tension versus time curve (Sams and Lucassen, to be published).

The following points summarise measured behaviour of surfactant solutions undergoing purely diffusional relaxation in time scales from \(10^{-2}\) to \(10^{+3}\) seconds:
Interfacial Viscoelasticity

(i) Numerical values of the viscoelastic modulus vary from 1 to 1000 mN/m, depending on surfactant parameters (concentration, adsorption characteristics) and on the rate of surface deformation used. Highest values are found for insoluble monolayer behaviour at fast deformation; at slower deformations viscosities of up to 200 mPa s have been found, but the contributions of these non-Newtonian viscosities to the total modulus values are extremely low.

(ii) Elasticity and viscosity values for any concentration and any rate of deformation can be predicted quantitatively if the surfactant’s equation of state is known.

Thus, the basic premises of diffusion, leading to eqs. 13-15, are fully confirmed by experimental results.

Other relaxation mechanisms relevant to emulsions and foams have been less comprehensively substantiated experimentally:

(i) Formation/dissolution of 3-D particles in collapsed monolayers of, e.g., long-chain alcohols, fatty acids, monoglycerides. Contrary to diffusion, this mechanism can produce high modulus values in combination with high viscous losses (Veer and van den Tempel, 1972).

(ii) Formation/dissolution of micelles in the bulk solution, leading to extremely low modulus values with very high viscous losses (Lucassen, 1975).

(iii) Noteworthy are the extremely high elasticity moduli combined with low viscous losses measured for DMPC/cholesterol monolayers, which have not been interpreted so far in terms of any specific relaxation mechanism (Lucassen-Reynders and Kuijpers, 1992).

Finally, almost all experimental data so far have been obtained at the air/water interface. The few published results for oil/water interfaces refer only to low-viscosity hydrocarbon oils, not to more viscous triacylglycerol oils.

Comparison with surface shear parameters

For small-molecule surfactants, surface shear viscosity as measured with various steady-state techniques such as the canal viscometer is generally very low, i.e., far below 1 mPa s (= 1 surface Poise). Higher values have been reported for macromolecular surfactants, e.g., proteins. As in compression/dilation, the elastic and viscous contributions to the shear modulus can be measured separately in an oscillatory experiment (de Feijter and Benjamins, 1979). Table I presents the dilational and shear properties measured under identical conditions of frequency and concentration for three proteins (Benjamins and van Voorst Vader, 1992). It is seen that in all three cases the dilational elasticity exceeds the shear elasticity, and in two out of three cases the dilational viscosity is also higher than the shear viscosity; the total modulus is always higher in compression/dilation than in shear.

Future Work Needed

For a full evaluation of surfactant effects in emulsions and foams, further work will be required in several areas:

(i) during the generation of emulsions and foams, interfacial elasticity and dynamic surface tension influence the break-up of large drops or bubbles. Experimental evidence for the effects of interfacial rheology on emulsion drop size obtained by break-up under practical conditions so far is qualitative (Lucassen-Reynders and Kuijpers, 1992). As illustrated in Figure 6, the numerical values of the rheological parameters very strongly depend on the local rates of area deformation. In most emulsifying machines, the local conditions of liquid flow, and hence these local surface deformation rates, are extremely variable. At this stage, our knowledge of such local variations is insufficient: realistic models need to be developed for controlled flow conditions in emulsifying machines.

(ii) Experimental and theoretical models must be set up for emulsifier effects on drop coalescence both during emulsification and afterwards. A practical example of coalescence long after emulsification is the oral behaviour of fat spreads, where coalescence is required as a preliminary to phase inversion after the solid fat has melted.

(iii) So far, experimental evidence of dynamic surface behaviour is virtually limited to the air/water surface. In some cases, theory for surface behaviour at air/water can be extrapolated to oil/water interfaces, but this is possible only for water-soluble surfactants, leading to oil-in-water emulsions. This leaves a gap in our knowledge of water-in-oil emulsifiers, which are crucial components of butter and other fat spreads. Monoacylglycerols and lecithins are examples of ubiquitous emulsifiers added to the oil phase of such products. Final product properties are known to be very sensitive to changes in molecular structure of these emulsifiers, e.g., the state of saturation of the hydrophobic chains. Such differences may be related to differences in the dynamic surface properties discussed here, but the experimental methods presently used are less suitable for these fairly viscous oil phases.

Theoretical evaluation can serve as an alternative to actual measurements in cases where we have independent information on the adsorption isotherms of emulsifiers at the oil/water interface. A numerical example is presented in Figures 12 and 13, for saturated and unsaturated monoacylglycerols (MAG). Adsorption isotherms for these emulsifiers can be estimated from measured interfacial tensions at equilibrium (Heerrije et al., 1990; Lucassen-Reynders and Kuijpers, 1992). The unsaturated compound more or less follows a Langmuir isotherm (eq. 6), with a fairly low limiting adsorption; the saturated compound deviates from this by following a Frumkin isotherm with a much higher limiting adsorption. This difference in adsorption can be understood from the different shapes of the molecules: the saturated straight chains can be much more closely packed at the interface, as illustrated in Figure 12. The effect of this on calculated dynamic surface properties for diffusion...
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Figure 12. Estimated adsorption isotherms of saturated and unsaturated monoacylglycerols (MAG) of average chain-length C₁₆, at the sunflowerseed oil/water interface, at room temperature. (---) limiting adsorptions.

Figure 13. Viscoelastic moduli \(|\varepsilon|\) as a function of surfactant concentration (c), according to eq. 15 with parameters evaluated from the adsorption isotherms of Figure 12; diffusion coefficient \(D = 10^{-11} \text{ m}^2/\text{s}\); rate of surface deformation \(\omega = 100/\text{s}\).

Conclusions

The presence of surface active materials as emulsifiers or foamers endows fluid interfaces with dilational viscoelasticity which is a significant factor in (i) any liquid flow near the interface and (ii) the stability of thin films separating emulsion drops or foam bubbles. Numerically, values of the viscoelasticity are found to vary over a wide range, depending on surfactant parameters and on local conditions of surface deformation. A quantitative framework is available for the evaluation of these rheological parameters and of the dynamic surface tension of surfactant solutions if the relaxation mechanism is diffusion; other relaxation mechanisms have been studied less comprehensively.

References

Interfacial Viscoelasticity


Discussion with Reviewers

D.T. Wasan: The dilational viscosity is defined in eq. 1 by the author as the measure of the surface tension gradient which produces extra flow resistance against surface dilation/compression of the surfactant interface and which depends on the diffusion and adsorption rate of the surfactant molecules. In my opinion, this flow resistance is not a viscous resistance by nature because it is the result of interfacial composition changes and mass transfer, and thus it is misleading to call it dilational “viscosity”. Another treatment of these phenomena exists also in the literature, which separates the compositional (surface tension gradient) and purely viscous resistances of the interface. See a recent discussion in: Interfacial Transport Processes and Rheology, by Edwards DA et al., Butterworth-Heinemann Publishers: Stoneham, MA, 1991.

Author: The claim of the parameter $\eta_d$ defined in eq. 1 to the status of “true viscosity” can be judged by examining its relationship with the energy dissipation. Any true viscosity should measure the rate at which mechanical energy put into the system is irreversibly lost through relaxation mechanisms operative in the system. In surface dilation/compression, work is done against surface tension forces; therefore, any relaxation mechanism that affects the surface tension can be expressed in a surface viscosity. Diffusion of molecules to and from the surface is such a mechanism, and it can be demonstrated that the resulting viscosity, $\eta_d$ in eq. 14, is indeed a pure loss modulus, i.e., it is proportional to the amount of mechanical energy dissipated as heat. For this reason, $\eta_d$ is a true viscosity in my opinion. Perhaps, the confusion arises from the fact that the energy is dissipated not in the surface proper but in the adjoining bulk phase(s). An analogous situation may be seen in the damping of surface waves: such damping is caused by the viscosity of the bulk liquid but this need not prevent us from using the term surface wave.