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### RÉSUMÉ

Nous avons obtenu de nouvelles équations constitutives pour les flux de diffusion et de chaleur ainsi que pour les viscosités de cisaillement et de dilatation à l'aide de la théorie Onsager pour la fonction de dissipation des excédents de surface. La contrainte de dilatation dépend de la diffusion de surfactant, des réactions chimiques à l'interface et de l'adsorption de contre-ions des phases. On procède à des expériences de mesure de la dilatation et de la détente en surface avec une solution de surfactants ayant une masse moléculaire élevée. Les données sont interprétées au moyen des équations rhéologiques proposées et on obtient des résultats concernant l'élasticité Gibbs et la viscosité de dilatation interfaciale.

Une nouvelle méthode permettant de déterminer la viscosité de cisaillement des monocouches de surfactants à faible masse moléculaire est décrite. Cette méthode est basée sur la mesure du coefficient de traînée d'une sphère d'un millimètre, attachée à l'interface. On compare les prévisions théoriques avec les données expérimentales.

### ABSTRACT

New constitutive equations for the surface diffusion and heat fluxes, shear and dilatational viscosities are obtained using the Onsager theory for the surface-excess dissipation function. The dilatational part of the constitutive relation contains contributions of the surfactant diffusion, interfacial chemical reactions and the adsorption of counter-ions from the bulk-phases. Experiments with solution of high-molecular mass surfactants consisting of surface expansion and stress relaxation measurement are carried out. The data are interpreted by means of the proposed rheological equations and results for the Gibbs elasticity and interfacial dilatational viscosity are obtained.

A new method for determination of the shear viscosity of low-molecular surfactant monolayers is described. The method is based on the measurement of the drag coefficient of a millimetre sized sphere, attached to the interface. The theoretical predictions, are tested against experimental data.

## INTERFACIAL RHEOLOGY AND EMULSION STABILITY

### 1. Introduction

The *short-term* stability of concentrated emulsions depends on the *rate of drainage* of the liquid out of the gaps (films) between the droplets (1,2). On the other hand, the *long-term* emulsion stability is determined by the *thermodynamic stability* of the films formed between the emulsion droplets (3,4). In both cases the interfacial elasticity and viscosity play an important role (5). The interfacial rheology is described in terms of postulated constitutive relations for the surface stress tensor (like the Boussinesq-Scriven and Marangoni laws) as well as for the diffusion and thermal fluxes (say, the Fick's law). Several semi-empirical models for the dilatational interfacial viscous stress are used in literature: linear dependence upon the rate-of-strain (5); linear dependence on the rate of relative deformation of adsorption monolayer (6); a complex Maxwell rheological model (7). Thus the experimental results (obtained e.g. by the surface wave or expanding drop method) are treated using various rheological models. Therefore, it is sometimes difficult to find a connection between data for the interfacial viscosity reported by different authors who apply different models. Our purpose below is to investigate how a general interfacial constitutive relation has to look like, starting from first principles.

We present a theoretical study of the non-linear thermodynamics of a mixture of surfactants in the presence of chemical reactions. In particular, we consider the case of an *adsorbed protein*, which can exist at the interface in two conformations, denoted as components *B* and *C*; the chemical reaction of the conformational change,  $B \leftrightarrow C$ , is taken into account. The Onsager theory for the surface-excess dissipation function is applied in order to obtain phenomenological relations for the surface diffusion and heat fluxes, and for the surface stress tensor. The latter involves the surface shear and dilatational viscosities. Experimental techniques for determining the dilatational and shear interfacial viscosities (with low molecular weight surfactants) are discussed briefly.

### 2. Mass, Momentum, and Energy Transport Equations in Bulk and Surface Phases

In order to keep the equations simpler we consider a mixture of two components, denoted by subscripts „a“ and „b“, in the bulk phase. The equations for conservation of the total mass and the mass of the individual components in the continuous three-dimensional media can be written in the following form (1,4,5)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad \frac{\partial \rho_a}{\partial t} + \nabla \cdot (\rho_a \mathbf{v} + \mathbf{j}_a) = 0, \quad \frac{\partial \rho_b}{\partial t} + \nabla \cdot (\rho_b \mathbf{v} + \mathbf{j}_b) = 0, \quad [1]$$

where  $\rho_a$  and  $\rho_b$  are the densities of the species *A* and *B*,  $\rho = \rho_a + \rho_b$  is the liquid mass density,  $\mathbf{v}_a$  and  $\mathbf{v}_b$  are the velocities of the components,  $\mathbf{v} = (\rho_a \mathbf{v}_a + \rho_b \mathbf{v}_b) / \rho$  is the mass-average velocity,  $\mathbf{j}_a = -\mathbf{j}_b = \rho_a (\mathbf{v}_a - \mathbf{v})$  is the flux density vector relative to  $\mathbf{v}$ .

The momentum transport equation in the bulk phase reads

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) = 0. \quad [2]$$

In Eq. [2] the bulk pressure tensor  $\mathbf{P}$  may be decomposed as  $\mathbf{P} = p\mathbf{I} + \mathbf{T}$ , where  $p$  is the thermodynamic pressure,  $\mathbf{I}$  is the unit tensor, and  $\mathbf{T}$  is the viscous stress tensor. For non-polar fluids the viscous stress tensor is symmetric (5).

The balance equation of total energy per unit mass,  $u$ , in the bulk phase is

$$\frac{\partial}{\partial t}(\rho u) + \nabla \cdot (\rho u \mathbf{v} + \mathbf{q} + \mathbf{P} \cdot \mathbf{v}) = 0 \quad [3]$$

(Ref. 5). The quantity  $u$  is defined to be a sum of the mechanical and the internal energy. The heat flux vector is  $\mathbf{q}$ , and  $\mathbf{P} \cdot \mathbf{v}$  is the flux of energy due to the mechanical work. From the fundamental thermodynamic equation of Gibbs (1) and from Eq. [3] one finds the bulk phase entropy balance:

$$\frac{\partial}{\partial t}(\rho s) + \nabla \cdot (\rho s \mathbf{v} + \mathbf{J}^v) = \dot{s}^v, \quad \mathbf{J}^v = \frac{1}{T} \mathbf{q} - \frac{\mu_a}{T} \mathbf{j}_a - \frac{\mu_b}{T} \mathbf{j}_b, \quad [4]$$

where  $T$  is the temperature,  $s$  is the entropy per unit mass,  $\mu_a$  and  $\mu_b$  are the bulk chemical potentials of the two components, and  $\mathbf{J}^v$  is the entropy flux. The rate of entropy production,  $\dot{s}^v$ , is calculated to be

$$\dot{s}^v = -\frac{\nabla \mathbf{v}}{T} : \mathbf{T} + \nabla \cdot \left( \frac{1}{T} \right) \cdot \mathbf{q} - \nabla \cdot \left( \frac{\mu_a}{T} \right) \cdot \mathbf{j}_a - \nabla \cdot \left( \frac{\mu_b}{T} \right) \cdot \mathbf{j}_b. \quad [5]$$

The Onsager theory provides well known relations between the thermodynamic fluxes and the forces in Eq. [5] (with the bulk laws of diffusion and heat transfer, and Newtonian rheology).

At an interface Eqs. [1]-[3] require specification of bulk diffusion and heat fluxes, as well as kinematic, dynamic and energy conditions. We consider macro-scale material fluid interfaces, at which the kinematic boundary conditions are (i) equal material velocities of the bulk and the surface; (ii) zero normal velocity to the interface (it is assumed here that no exchange of mass occurs between the interface and contiguous bulk fluid).

Let us now consider a mixture of three components in the *surface* phase: solvent ( $A$ ), surfactant ( $B$ ) (present also in the bulk), and surfactant ( $C$ ), which is insoluble in the volume phases and is a product of a chemical reaction at the interface. For example, such is the case of a surface active protein  $B$  which may change its conformation to a final form  $C$ . Then, the equations of interfacial species transport read (5)

$$\begin{aligned} \frac{\partial \rho_a^s}{\partial t} + \nabla_s \cdot (\rho_a^s \mathbf{v}_\tau + \mathbf{j}_a^s) &= j_a^{vs}, & \frac{\partial \rho_b^s}{\partial t} + \nabla_s \cdot (\rho_b^s \mathbf{v}_\tau + \mathbf{j}_b^s) &= R_b + j_b^{vs}, \\ \frac{\partial \rho_c^s}{\partial t} + \nabla_s \cdot (\rho_c^s \mathbf{v}_\tau + \mathbf{j}_c^s) &= R_c, & \frac{\partial \rho^s}{\partial t} + \nabla_s \cdot (\rho^s \mathbf{v}_\tau) &= 0, \end{aligned} \quad [6]$$

where  $\nabla_s$  is the surface gradient operator; the surface-excess species mass densities are defined by  $\rho_a^s = M_a \Gamma_a$ ,  $\rho_b^s = M_b \Gamma_b$ , and  $\rho_c^s = M_c \Gamma_c$  ( $\Gamma_a$ ,  $\Gamma_b$  and  $\Gamma_c$  are the adsorptions of  $A$ ,  $B$  and  $C$ ,  $M_a$ ,  $M_b$  and  $M_c$  are the molar masses);  $\rho^s$  is the surface-excess mass density;  $\mathbf{v}_\tau$  is the surface velocity, which is equal to the tangential component of the bulk velocity at the interface;  $R_b = -R_c$  is the species production rate due to the surface chemical reaction. The surface diffusion fluxes are defined by the expressions  $\mathbf{j}_b^s = \rho_b^s (\mathbf{v}_b - \mathbf{v})_\tau$ ,  $\mathbf{j}_c^s = \rho_c^s (\mathbf{v}_c - \mathbf{v})_\tau$ ,  $\mathbf{j}_a^s = -(\mathbf{j}_b^s + \mathbf{j}_c^s)$ . Eqs. [6] provide the boundary condition imposed upon the normal component of the bulk-phase species flux at the interface,  $j_a^{vs} = -j_b^{vs}$ .

The equation of momentum transport (without external surface forces) is:

$$\frac{\partial}{\partial t}(\rho^s \mathbf{v}_\tau) + \nabla_s \cdot (\rho^s \mathbf{v}_\tau \mathbf{v}_\tau + \mathbf{P}^s) = \mathbf{n} \cdot \mathbf{P}^{vs}, \quad [7]$$

where  $\mathbf{P}^s$  is the interfacial pressure tensor and  $\mathbf{n}$  is the unit normal to the mathematical surface. A general decomposition of  $\mathbf{P}^s$  may be made in terms of static and viscous parts:  $\mathbf{P}^s = -\sigma \mathbf{I}^s + \mathbf{T}^s$ ,

where  $\mathbf{I}^s$  is the two-dimensional idemfactor,  $\sigma$  is the interfacial tension and  $\mathbf{T}^s$  is the surface viscous stress tensor. Eq. [7] provides the boundary condition imposed upon the normal component of the contiguous bulk-phase pressure tensor  $\mathbf{n} \cdot \mathbf{P}^{vs}$  at the interface.

The balance equation of total surface energy per unit mass,  $u^s$ , reads (5)

$$\frac{\partial}{\partial t}(\rho^s u^s) + \nabla_s \cdot (\rho^s u^s \mathbf{v}_\tau + \mathbf{q}^s + \mathbf{P}^s \cdot \mathbf{v}_\tau) = q^{vs} + \mathbf{n} \cdot \mathbf{P}^{vs} \cdot \mathbf{v}_\tau, \quad [8]$$

which is a counterpart of Eq. [3]. In Eq. [8]  $\mathbf{q}^s$  is the surface heat flux, and  $q^{vs} = \mathbf{n} \cdot \mathbf{q}^{vs}$  is the normal component of the contiguous bulk-phase heat flux. The term in the right hand side of Eq. [8] is the flux of the total energy from the bulk phase. The respective equation for the surface *internal* energy may be derived from Eq. [8]. Then, using the fundamental thermodynamic Gibbs equation (1), one ends up with the two-dimensional analogue of the bulk entropy balance:

$$\frac{\partial}{\partial t}(\rho^s s^s) + \nabla_s \cdot (\rho^s s^s \mathbf{v}_\tau + \mathbf{J}^s) = \frac{1}{T^{vs}} q^{vs} - \frac{\mu_a^{vs}}{T^{vs}} j_a^{vs} - \frac{\mu_b^{vs}}{T^{vs}} j_b^{vs} + \dot{s}^s. \quad [9]$$

In Eq. [9]  $s^s$  is the surface entropy per unit mass,  $T^{vs}$  is the temperature in the contiguous bulk phase, and  $\mu_a^{vs}$ ,  $\mu_b^{vs}$  are the chemical potentials of solvent (A) and surfactant (B) in the bulk. The surface entropy flux,  $\mathbf{J}^s$ , is defined by the expression  $T^s \mathbf{J}^s = \mathbf{q}^s - \mu_a^s \mathbf{j}_a^s - \mu_b^s \mathbf{j}_b^s - \mu_c^s \mathbf{j}_c^s$ . The temperature and the chemical potentials per unit mass in the interfacial phase are  $T^s$ ,  $\mu_a^s$ ,  $\mu_b^s$ , and  $\mu_c^s$ . For the rate of entropy production per unit area of the material surface,  $\dot{s}^s$ , we derive:

$$\begin{aligned} \dot{s}^s = & -\frac{\nabla_s \mathbf{v}_\tau : \mathbf{T}^s}{T^s} - \frac{\nabla_s T^s}{(T^s)^2} \cdot \mathbf{q}^s - \frac{\nabla_s (\mu_b^s - \mu_a^s)}{T^s} \cdot \mathbf{j}_b^s - \frac{\nabla_s (\mu_c^s - \mu_a^s)}{T^s} \cdot \mathbf{j}_c^s - \\ & - \left( \frac{1}{T^{vs}} - \frac{1}{T^s} \right) q^{vs} - \frac{\mu_b^s - \mu_c^s}{T^s} R_b - \left( \frac{\mu_b^s - \mu_a^s}{T^s} - \frac{\mu_b^{vs} - \mu_a^{vs}}{T^{vs}} \right) j_b^{vs}, \end{aligned} \quad [10]$$

The Onsager theory provides necessary relations between the thermodynamic fluxes and the forces.

### 3. Onsager Theory for Two-Dimensional Continua

From thermodynamic viewpoint, the rate of entropy production is the surface dissipation function and is positive for all values of the thermodynamic forces. Then, each scalar product of the tensors, vectors and scalars in Eq. [10] must be positive.

The deviatoric part of the surface-excess viscous stress tensor may be written in the form

$$\mathbf{T}^s - \frac{1}{2}(\mathbf{I}^s : \mathbf{T}^s) \mathbf{I}^s = -\mathbf{E}_{sh} \cdot \left[ \mathbf{D}^s - \frac{1}{2}(\mathbf{I}^s : \mathbf{D}^s) \mathbf{I}^s \right], \quad \mathbf{D}^s = \frac{1}{2} \left[ \nabla_s \mathbf{v}_\tau \cdot \mathbf{I}^s + \mathbf{I}^s \cdot (\nabla_s \mathbf{v}_\tau)^T \right], \quad [11]$$

where  $\mathbf{D}^s$  is the surface rate-of-strain tensor and  $\mathbf{E}_{sh}$  is the interfacial shear viscosity tensor. In the case of isotropic interface the trace of  $\mathbf{E}_{sh}$  defines the interfacial shear viscosity,  $\eta_{sh}$ .

In the frames of the Onsager's theory, the surface thermodynamic fluxes in Eq. [10] are represented as linear superpositions of surface thermodynamic forces:

$$\mathbf{q}_{tot}^s = -L_{qq}^{vv} \frac{\nabla_s T^s}{(T^s)^2} - L_{bq}^{vv} \frac{\nabla_s (\mu_b^s - \mu_a^s)}{T^s} - L_{cq}^{vv} \frac{\nabla_s (\mu_c^s - \mu_a^s)}{T^s},$$

$$\mathbf{j}_b^s = -L_{bq}^{vv} \frac{\nabla_s T^s}{(T^s)^2} - L_{bb}^{vv} \frac{\nabla_s (\mu_b^s - \mu_a^s)}{T^s} - L_{bc}^{vv} \frac{\nabla_s (\mu_c^s - \mu_a^s)}{T^s}, \quad [12]$$

$$\mathbf{j}_c^s = -L_{cq}^{vv} \frac{\nabla_s T^s}{(T^s)^2} - L_{bc}^{vv} \frac{\nabla_s (\mu_b^s - \mu_a^s)}{T^s} - L_{cc}^{vv} \frac{\nabla_s (\mu_c^s - \mu_a^s)}{T^s}.$$

The phenomenological matrix of coefficients,  $\mathbf{L}$ , includes the surface heat transfer coefficient, the thermo-diffusion coefficients of the surfactant species, and the surface diffusion coefficients. Therefore: (i) the surface heat transfer flux may be expressed as a sum of a heat transfer due to the surface temperature gradient and molecular diffusive heat fluxes; (ii) the surface species flux is a sum of the surface thermal diffusive flux and the molecular diffusive fluxes.

The phenomenological relations for the isotropic part of the surface-excess viscous stress tensor and for the scalar quantities in Eq. [10] read:

$$\frac{\mathbf{I}^s : \mathbf{T}^s}{2} = -\frac{L_{vv}^{cc}}{T^s} \dot{\alpha} - L_{vq}^{cc} \left( \frac{1}{T^{vs}} - \frac{1}{T^s} \right) - \frac{L_{vr}^{cc}}{T^s} \left[ (\mu_b^s - \mu_a^s) - (\mu_c^s - \mu_a^s) \right] - L_{vd}^{cc} \left( \frac{\mu_b^s - \mu_a^s}{T^s} - \frac{\mu_b^{vs} - \mu_a^{vs}}{T^{vs}} \right) \quad [13.1]$$

$$\mathbf{q}^{vs} = -\frac{L_{vq}^{cc}}{T^s} \dot{\alpha} - L_{qq}^{cc} \left( \frac{1}{T^{vs}} - \frac{1}{T^s} \right) - \frac{L_{qr}^{cc}}{T^s} \left[ (\mu_b^s - \mu_a^s) - (\mu_c^s - \mu_a^s) \right] - L_{qd}^{cc} \left( \frac{\mu_b^s - \mu_a^s}{T^s} - \frac{\mu_b^{vs} - \mu_a^{vs}}{T^{vs}} \right) \quad [13.2]$$

$$R_b = -\frac{L_{vr}^{cc}}{T^s} \dot{\alpha} - L_{qr}^{cc} \left( \frac{1}{T^{vs}} - \frac{1}{T^s} \right) - \frac{L_{rr}^{cc}}{T^s} \left[ (\mu_b^s - \mu_a^s) - (\mu_c^s - \mu_a^s) \right] - L_{rd}^{cc} \left( \frac{\mu_b^s - \mu_a^s}{T^s} - \frac{\mu_b^{vs} - \mu_a^{vs}}{T^{vs}} \right) \quad [13.3]$$

$$j_b^{vs} = -\frac{L_{vd}^{cc}}{T^s} \dot{\alpha} - L_{qd}^{cc} \left( \frac{1}{T^{vs}} - \frac{1}{T^s} \right) - \frac{L_{rd}^{cc}}{T^s} \left[ (\mu_b^s - \mu_a^s) - (\mu_c^s - \mu_a^s) \right] - L_{dd}^{cc} \left( \frac{\mu_b^s - \mu_a^s}{T^s} - \frac{\mu_b^{vs} - \mu_a^{vs}}{T^{vs}} \right). \quad [13.4]$$

Therein,  $\dot{\alpha} = d \ln(\delta A) / dt = \nabla_s \cdot \mathbf{v}_\tau$  is the rate of total deformation of the interfacial area  $\delta A$ . The relations [13] show that the surface deformation, the difference between the subsurface and surface temperature (in the case of surface heat sources), and the chemical potential differences (with respect to the solvent) are the main factors for the deviation from equilibrium.

In order to make our conclusions simpler, we consider Eqs. [13.1] and [13.3] in the particular case of isothermal processes. Then, in the absence of surface chemical reactions, the type of the rheological relation for the dilatational viscous stress depends on the adsorption kinetics. For diffusion-controlled adsorption the *equilibrium* isotherm may be used, which is equivalent to  $\mu_b^s - \mu_a^s = \mu_b^{vs} - \mu_a^{vs}$ . For barrier-controlled adsorption the stage of surfactant transfer from the subsurface to the surface is much slower than the diffusion. The adsorption barrier can be due to steric hindrance, electrostatic repulsion or conformational changes accompanying the adsorption of the molecules. Then, the difference between the chemical potentials is determined by the difference between the rate of surfactant adsorption and desorption. Consequently, the Boussinesq-Scriven law is not adequate for description of the relation between the surface viscous stress and the thermodynamic forces. The same situation realises in the presence of surface chemical reactions, when the additional phenomenological equation [13.3] for the surface species production rate,  $R_b$ , closes the problem.

#### 4. Methods for Determination of the Dilatational and Shear Surface Viscosities

The basis of the interfacial rheology is the constitutive relation for the interfacial pressure tensor,  $\mathbf{P}^s$ . From the definition of  $\mathbf{P}^s$  (Section 2) and from Eq. [11] there follows

$$\mathbf{P}^s = -(\sigma + \tau_{dil})\mathbf{I}_s - 2\eta_{sh}\left(\mathbf{D}_s - \frac{1}{2}\mathbf{I}_s\nabla_s \cdot \mathbf{v}_\tau\right), \quad [14]$$

with  $\tau_{dil}$  being the dilatational interfacial viscous stress, measured in processes of isotropic expansion (compression) of the surface. Such processes take place in the maximum bubble pressure method, the oscillating bubble method, the pulsed drop method, and the drop expanding method (1,5,6). In all these cases the system possesses simple spherical symmetry. Then, Eq. [14] together with the normal projection of Eq. [7] yields  $\sigma(t) + \tau_{dil}(t) = R(t)(p_1 - p_2)/2$ , where  $p_1$  and  $p_2$  are the pressures inside and outside the droplet or bubble, and  $R$  is its radius. For small deformations  $\sigma$  depends linearly on the local strain and one can write

$$\sigma = \sigma_e + E_G^b \varepsilon_b + E_G^c \varepsilon_c, \quad \varepsilon_b \equiv -\frac{\delta\Gamma_b}{\Gamma_b}, \quad \varepsilon_c \equiv -\frac{\delta\Gamma_c}{\Gamma_c}, \quad E_G^b \equiv -\left(\frac{d\sigma}{d\ln\Gamma_b}\right)_{\Gamma_c}, \quad E_G^c \equiv -\left(\frac{d\sigma}{d\ln\Gamma_c}\right)_{\Gamma_b}, \quad [15]$$

where  $\sigma_e$  is the equilibrium interfacial tension,  $\varepsilon_b$  and  $\varepsilon_c$  express the relative dilatation of the adsorption monolayers of components  $B$  and  $C$ , and  $E_G^b$ ,  $E_G^c$  are the respective Gibbs elasticities. For isothermal isotropic process, from Eqs. [13.3] and [13.4] we can calculate the differences between the chemical potentials as functions of  $R_b$ ,  $j_b^{vs}$  and the total deformation of the interfacial area. Using the equation of interfacial species transport [6], written in the form  $R_b + j_b^{vs} = \rho_b^s(\dot{\alpha} - \dot{\varepsilon}_b)$  and  $R_c + j_c^{vs} = \rho_c^s(\dot{\alpha} - \dot{\varepsilon}_c)$ , we derive an expression for the dilatational surface viscous stress:  $\tau_{dil} = \eta_d^a \dot{\alpha} + \eta_d^b \dot{\varepsilon}_b + \eta_d^c \dot{\varepsilon}_c$ , where the parameters  $\eta_d^a$ ,  $\eta_d^b$ , and  $\eta_d^c$  represent *true* surface dilatational viscosities (in contrast to the *apparent* viscosities due to additional dissipation processes, as introduced for example in the experimental methods with surface waves). In fact, utilizing the measured pressure inside the expanding droplet (bubble) and its radius, one can write

$$E_G^b \varepsilon_b + E_G^c \varepsilon_c + \eta_d^a \dot{\alpha} + \eta_d^b \dot{\varepsilon}_b + \eta_d^c \dot{\varepsilon}_c = \frac{1}{2} [R(t)\Delta p(t) - R(0)\Delta p(0)], \quad \Delta p \equiv p_1 - p_2. \quad [16]$$

In addition,  $\dot{\alpha}$  can also be determined experimentally, from the recorded expansion of the droplet (bubble). However, for soluble surfactants it is very difficult to measure the local deformations directly, and then the theoretical treatment developed in Ref. 6 may be applied. It should be noted that for low molecular weight surfactants the viscous term in Eq. [16] is usually negligible. The diffusion relaxation of the local deformation is predominant, instead of a real surface viscous friction. Therefore, from such a relaxation process one can determine the diffusion relaxation time, rather than a true surface dilatational viscosity.

Eq. [16] can be used to interpret results from expansion-relaxation experiments. In principle, by fitting data for the interfacial dilatation one can obtain values for the Gibbs elasticity, the diffusion relaxation time, and the dilatational surface viscosity. The latter quantity is accessible only for high molecular weight surfactants and proteins, due to the limited accuracy of the aforementioned experimental techniques. Sometimes, the surface dilatational viscosities can be determined also for low molecular weight anionic surfactants, but in the presence of multivalent counterions (like  $\text{Ca}^{2+}$  or  $\text{Al}^{3+}$ ), which link neighboring surfactant headgroups together.

A typical experiment, described in Ref. 6, consists of the following three stages: (i) initial formation of a saturated surfactant adsorption layer at the interface, keeping the drop area constant for several hours; (ii) fast expansion of the adsorption layer by increasing the drop area for several seconds; (iii) relaxation of the expanded adsorption layer under constant drop area. Experimental data for bovine serum albumin (BSA) at decane-water interface (6) have shown that the pH and the ionic strength influence the rheological properties of the protein: both the surface elasticity and the

relaxation time increase with rising pH; the interfacial dilatational viscosity exhibits a maximum at pH=6. A similar peak of the interfacial shear viscosity of BSA at pH=6 has been observed by Graham and Phillips (8) at petroleum ether/ water interface.

A new method for measuring low surface *shear* viscosities is described in Refs. (9,10). This method is based on recording the sliding of a small spherical particle down an inclined capillary meniscus formed in the vicinity of a vertical plate. The theory of the method employs accurate expressions for the capillary force exerted on the floating particle (11,12), which is counterbalanced by the hydrodynamic drag force (13). The experiment (10) gives values of the drag coefficient which are in good quantitative agreement with the hydrodynamic theory for pure liquids (13). The addition of surfactant strongly increases the drag coefficient. The latter effect is used to measure the surface viscosity ( $\eta_{sh} \geq 10^{-6}$  Pa.m.s) of low molecular weight surfactants, like SDS or Brij. In such systems the values of  $\eta_{sh}$  are not accessible by most of the conventional methods (e.g., deep-channel and disk surface viscometers, knife-edge viscometers).

### 5. Conclusions

This work offers a general result for the rate of entropy production on an interface covered by surfactant mixture, in the presence of surface chemical reaction. The Onsager theory is applied to obtain phenomenological relations for the surface diffusion and heat fluxes, shear and dilatational viscosities, production rate of the components. Rigorous expression for the dilatational surface viscous stress answers the question how to account for the "true" interfacial viscous effects (which are due to energy dissipation) in the rheology of surfactant adsorption layers.

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