

# Interfacial rheology of adsorbed layers with surface reaction: On the origin of the dilatational surface viscosity

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## Abstract

A theoretical study of the phenomena, occurring in an adsorbed layer, subject to small dilatational perturbations was carried out. Two main processes, provoked by the perturbations (surface reaction and surfactant transport onto the surface) were considered. The reaction was described by means of the reaction coordinate. The derived general rheological equation for insoluble surfactants, gave as limiting cases Voight and Maxwell type equations for fast and slow reactions, respectively. Expressions for all characteristics of the process (surface elasticity, reaction elasticity, reaction relaxation time and dilatational surface viscosity) were obtained. The obtained generalized rheological equation for reactions involving soluble surfactants is a dynamic analog of Gibbs adsorption isotherms for a multi-component system with surface reaction, since similarly to Gibbs equation it relates the surface stress only to surface variables. It gives as limiting cases generalized forms for soluble surfactants of Voight and Maxwell equations. All new rheological equations were analyzed for deformations with constant rate and periodic oscillations and they were applied to three simple surface reactions (monomolecular with one product, dimerization and association). The mass transfer was analyzed initially in the absence of surface reaction. In this system the surface stress is purely elastic, but it was shown that if the adsorption perturbation is small, regardless of the type of surface perturbation and the mechanism of adsorption, the process of mass transport always obeys a Maxwell type rheological equation. For all considered processes surface viscosities were defined, but they were called “apparent”, because they stem from diffusion, rather than from interaction between the surfactant molecules and they depend not only on surface parameters, but also on the geometry of the system. The often used in the literature correlations between the lifetime of emulsions and foams and the imaginary elasticity were analyzed. It was shown that this approach lacks serious scientific foundations and could lead to erroneous conclusions. Finally, the problem for the coupling of the surfactant diffusion with the chemical reaction was analyzed and it was demonstrated on a simple example how it could be tackled.

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*Keywords:* Interfacial rheology; Surface reaction; Insoluble and soluble surfactants; Surface viscosity; Surface elasticity; Maxwell and Voight laws; Role of diffusion; Oscillations and continuous deformation of surfaces

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## 1. Introduction

In most cases of practical interest, the interfaces separating two bulk fluid phases are covered by insoluble or (more often) soluble surfactants. Under dynamic conditions the adsorbed layer undergo deformations, which lead to the appearance of surface stresses. These stresses cause a jump in the values of the viscous stresses, exerted on the surface by the bulk fluids, thus modifying significantly the behavior of the system. This fact affects the occurrence of many important processes such as drop (or bubble) formation, motion, deformation and break up, jet beak up, surface waves damping, kinetics of wetting and spreading and most importantly—the interaction and coalescence between drops and bubbles [1–8] and thereby—the formation and lifetime of emulsions and foams. The surface stresses affect strongly also the interaction and the attachment of bubbles to solid particles, which is the most important stage of the flotation process [9].

There are two types of surface stresses: elastic and viscous (see below). The viscous stresses can be represented as originating from two types of deformation [10]: shear and dilatation. The coefficients characterizing these stresses are called surface (interfacial) viscosities: surface shear viscosity,  $\eta_s^{\text{sh}}$ , and surface dilatational viscosity,  $\eta_s^{\text{dil}}$ , respectively for the two types of deformation. The interfacial shear viscosity,  $\eta_s^{\text{sh}}$ , is a well-defined quantity. Probably the main reason for this is the fact, that when the adsorbed layer is subject to shear, the adsorption does not change along the surface (since the area remains constant), so that the bulk solution has little effect on the processes occurring at the interface. In this case even for soluble surfactants the surface can be treated as an autonomous phase, similarly to a bulk phase. The origin of the surface shear viscosity is similar to that of the bulk viscosity—for simple surfactants it is taught to be due to jumps of the molecules from one equilibrium position to another [11,12] and for adsorbed polymers and proteins, it is ascribed also to changes of the conformations and interactions of the molecules, induced by the shear

stress [13,14]. We will confine ourselves in this article only with the surface dilatational viscosity, which we will call for brevity “surface viscosity” and will denote by  $\eta_s$ . Unlike its shear counterpart, it does not have exact definition in the literature and in many cases the reported experimental values depend on the models used for interpretation of the data obtained in surface rheological experiments. The most popular dilatational rheological laws are briefly discussed below.

Due to the deformation (expansion and/or contraction) of the interface, the surface area,  $A$ , is a function of time,  $t$ . Let us assume for simplicity that the experiments start from an equilibrium state of the investigated system with initial surface area  $A_0$  and that the time dependence,  $A=A(t)$ , is known. The rate of surface deformation,  $\dot{\alpha}(t)$ , and the surface deformation,  $\alpha$ , are defined as [15–18]:

$$\dot{\alpha}(t) \equiv \frac{1}{A} \frac{dA}{dt} = \frac{d\alpha(t)}{dt}, \quad \alpha(t) = \int_0^t \dot{\alpha} dt = \ln \frac{A(t)}{A_0} \approx \frac{\Delta A}{A_0} \quad (1.1)$$

where  $\Delta A(t)=A(t)-A_0$ .

The surface stress,  $\tau_s(t)$ , is defined as the difference between the initial surface pressure at equilibrium,  $\pi_{\text{eq}}$ , and the instantaneous value of the surface pressure,  $\pi(t)$  [15–18]:

$$\tau_s(t) \equiv \pi_{\text{eq}} - \pi(t) \quad (1.2)$$

The dependence of the surface stress on the surface deformation,  $\alpha(t)$ , and on the rate of surface deformation,  $\dot{\alpha}(t)$ , is called rheological constitutive equation.

The reasons lying behind the main rheological equations can be understood by means of the following considerations. Imagine that we have changed the area of a layer with  $N_0$  adsorbed molecules of insoluble surfactant from  $A_0$  to  $A=A_0+\Delta A$ , where  $\Delta A \ll A_0$ . At that the adsorption,  $\Gamma \equiv N_0/A$ , will become  $\Gamma = N_0/(A_0+\Delta A) \approx \Gamma_{\text{eq}}(1-\alpha)$ , i.e. it will change by  $\tilde{\Gamma} = \Gamma - \Gamma_{\text{eq}} = -\Gamma_{\text{eq}}\alpha$ , where  $\Gamma_{\text{eq}}$  is the initial adsorption. Since the surface pressure,  $\pi$ , is function of  $\Gamma$ , in

the new equilibrium state it will become  $\pi(\Gamma)$ . The difference between the surface pressures,  $\pi(\Gamma_{\text{eq}}) - \pi(\Gamma)$ , is the elastic stress,  $\tau_{\text{el}}$ , needed to change the area by  $\Delta A \ll A_0$ :

$$\tau_{\text{el}} = \pi_{\text{eq}} - \pi(\Gamma) = - \left( \frac{\partial \pi}{\partial \Gamma} \right)_{\text{eq}} \Gamma_{\text{eq}} \frac{\dot{\Gamma}}{\Gamma_{\text{eq}}} = E_G \alpha, \quad E_G \equiv \left( \frac{\partial \pi}{\partial \ln \Gamma} \right)_{\text{eq}} \quad (1.3)$$

This is an elastic deformation since the stress is proportional to  $\Delta A/A_0$ . The quantity,  $E_G$ , is called accordingly Gibbs (surface) elasticity.

The surface deformation is related to rearrangement of the molecules, which perform Brownian motion and interact with each other. Let the rearrangement process is characterized by a characteristic time  $t_r$ , needed for the molecules to take their new positions upon deformation (including also to form new substances if it is possible). If we shrink the surface with rate  $\dot{\alpha}$ , the characteristic time of deformation will be  $t_{\text{def}} = 1/\dot{\alpha}$ . In a quasi-static (infinitely slow) process,  $t_{\text{def}} \gg t_r$ , and the molecules have enough time to reach their new equilibrium positions, so that the system is virtually at equilibrium during the entire process. Eq. (1.3) corresponds to such process.

The situation will change if we want to perform the surface deformation with finite speed, whose characteristic time is comparable to or smaller than  $t_r$ . Then the molecules have less time to reach the new equilibrium positions and since  $t_r$  is the same (it depends only on the properties of the system, not on  $t_{\text{def}}$ ) the rearrangement will lag behind the deformation. If we want to maintain the speed  $\dot{\alpha}$ , we must exert an extra stress [in addition to the elastic stress (1.3)] to force the molecules to go quickly to their new positions, corresponding to the deformation  $\alpha$ . This extra stress is called viscous stress,  $\tau_{\text{visc}}$ . The faster the deformation, the larger the viscous stress must be. More precisely, the viscous stress will depend on the ratio  $t_r/t_{\text{def}}$ , where  $t_{\text{def}} = 1/\dot{\alpha}$  is the characteristic time of the deformation. If we are not too far away from equilibrium, the viscous stress will be proportional to the deformation rate, i.e.  $\tau_{\text{visc}} = \eta_s \dot{\alpha}$ . The proportionality coefficient  $\eta_s$  is the dilatational surface viscosity. The situation is the same with the opposite process, expansion. Again the molecules need time to occupy the new positions and must be forced to do it quickly. Therefore, again an extra (viscous) stress is needed to perform the process in finite time.

The work performed by the viscous stress for the deformation,  $\alpha$ , is entirely dissipated, usually as heat. Indeed, the work done on a system to move it between two equilibrium states in an isothermal quasi-static process is equal to the change of its Helmholtz free energy and does not depend on the selected path between the states. Since the elastic process between the equilibrium states with  $\pi_{\text{eq}}$  and  $\pi(\Gamma)$  is also quasi-static, only the work done by the elastic stress can be stored by the system as free energy. Therefore,

the work done by the viscous stress will be lost, i.e. will be fully dissipated. Since the rate of energy dissipation depends on the square of the deformation rate [10] the dissipated energy will be always positive, regardless of the direction of the process. This means also that the surface viscosity must be always positive. By summing up the two stresses, we obtain the total surface stress,  $\tau_s$ , as a function of the deformation,  $\alpha$ , (called often strain) and of its rate,  $\dot{\alpha}$ , (called also rate of strain). The respective constitutive law was proposed by Kelvin [19] and Voight (see e.g. [20]) provided the mathematical expression of Kelvin's idea. Since the values of the elasticity and the surface viscosity depend often on the model used, for the Voight model we will denote them by  $E_V$  and  $\eta_V$ , respectively. Thus the Voight equation is:

$$\tau_s = E_V \alpha + \eta_V \dot{\alpha} \quad (1.4)$$

Another rheological equation was proposed by Maxwell [21]. He modeled the process of deformation by a purely elastic and a purely viscous element with elasticity  $E_M$  and viscosity  $\eta_M$ , respectively. He assumed that the elements are connected in series and subject to a stress  $\tau_s$ , leading to an elastic deformation  $\alpha_{\text{el}} = \tau_s/E_M$  with rate  $\dot{\alpha}_{\text{el}} = \dot{\tau}_s/E_M$  and a viscous deformation with rate  $\dot{\alpha}_{\text{visc}} = \tau_s/\eta_M$  (the dot means differentiation with respect of time,  $t$ ). He assumed also that the rate of total deformation is  $\dot{\alpha} = \dot{\alpha}_{\text{el}} + \dot{\alpha}_{\text{visc}}$ , which leads directly to his equation:

$$\frac{\dot{\tau}_s}{E_M} + \frac{\tau_s}{\eta_M} = \dot{\alpha} \quad (1.5)$$

Voight model is also often represented as composed of one elastic element with  $\tau_{\text{el}} = E_V \alpha$  and one viscous with  $\tau_{\text{visc}} = \eta_V \dot{\alpha}$ , which are however connected in parallel, so that  $\tau_s = \tau_{\text{el}} + \tau_{\text{visc}}$ .

In the Voight model the surface is considered in fact as a compressible two-dimensional fluid. Indeed, the Voight Eq. (1.4) is exact analog of the change of the normal stress  $p_{\text{nn}}$  in a compressible fluid with zero shear viscosity [10]:

$$p_{\text{nn}} = -p + \eta_b^{\text{dil}} \nabla \cdot \mathbf{v} \quad (1.6)$$

where  $p$  is pressure,  $\nabla$  is the spatial gradient operator,  $\mathbf{v}$  is the velocity vector and  $\eta_b^{\text{dil}}$  is the bulk dilatational viscosity, called also "second viscosity" [10]. For small volume deformations,  $\Delta V$ , one can write

$$p = p_0 + \left( \frac{\partial p}{\partial V} \right)_0 \Delta V = p_0 - E_b \alpha_b \quad (1.7)$$

where  $\alpha_b \approx \Delta V/V_0$  is the deformation,  $p_0 = -p_{\text{nn}}(\Delta V=0)$ —the equilibrium pressure and  $E_b \equiv -(\partial p/\partial \ln V)_0$ —the bulk elasticity. The expression  $\nabla \cdot \mathbf{v}$  is nothing else but the relative rate of deformation in the bulk,  $\dot{\alpha}_b$  [10,15,16]. Thus from Eq. (1.6) one obtains:

$$\tau_n = p_{\text{nn}} - p_{\text{nn}}(0) = E_b \alpha_b + \eta_b^{\text{dil}} \dot{\alpha}_b \quad (1.8)$$

which is the bulk counterpart of Voight equation.

The term  $\eta_b^{\text{dil}}\dot{\alpha}_b$  in Eq. (1.8) leads to the appearance in Navier–Stokes equation of a term  $\eta_b^{\text{dil}}\nabla(\nabla\cdot\mathbf{v})$ , which is zero for incompressible liquids, so that the contribution of  $\eta_b^{\text{dil}}$  vanishes. Since all liquids behave as incompressible under normal experimental conditions, for very long time the bulk dilatational viscosity of liquids was simply ignored. Only around the middle of the 20th century the advent of high frequency acoustic methods made possible the study of the dilatational viscosity (for theories, experimental methods and results see e.g. [22]). The measured values of  $\eta_b^{\text{dil}}$  turned out to be always very close to the shear bulk viscosity,  $\eta_b^{\text{sh}}$ , for the same liquid or molten metal. This is due to the fact that in liquids the dilatational viscosity is almost entirely due to the so-called structural viscosity. The latter is related to the change of structure of the liquids with the change of volume. Hall [23] applied the theory of Bernal and Fowler [24], according to which the liquids consist of “icebergs” of one liquid floating in another liquid, the difference between those liquids being entirely due to their structure and density. Hall [23] argued that upon compression the less dense liquid is transformed into the more dense one, this process leading to dissipation of energy and thereby—to the appearance of dilatational viscosity. Hirai and Eyring [25] assumed existence of holes (vacancies) in the liquids—applying pressure on the liquid forces the atoms, surrounding a hole to “jump” to new positions in order to fill the holes and increase the density. Since the shear viscosity is due to similar forced “jumps” of the molecules from one equilibrium position to another [11,12], the authors simply modified Eyring’s theory of the shear viscosity by accounting for the presence of holes and for the liquid compressibility. It should be obvious then, why the shear and dilatational (structural) viscosity of liquids have similar values.

Such structural viscosity may indeed exist in an adsorbed layer, but it should become noticeable only very near the complete surface coverage. At the same time, the surface (Gibbs) elasticity rises steeply with the surface coverage and in dense monolayers completely dominates the rheological surface behavior. That is why we believe that for some adsorbed layers another process can lead to more important dissipation of energy at moderate surface coverage—the occurrence of surface reactions. Such mechanism was suggested by Mandelstam (see [10], Ch. 8), who showed that some chemical reactions, accompanied with volume change, lead to energy dissipation, equivalent to a bulk dilatational viscosity. It seems pertinent to call this component of the dilatational viscosity chemical viscosity. In Section 2 we will apply this idea to a mixed monolayer of insoluble surfactants.

When the surfactants are soluble, the surface is no longer an autonomous phase and  $\alpha$  and  $\alpha'$  are not the only factors determining the instantaneous state of the monolayer. The surface composition can change also due to the exchange of soluble surfactants with the contiguous phases. These changes will be different for every component. Let  $\Delta N_k$

be the change of the total number of molecules at the surface of the component  $k$ , due only to mass exchange with the bulk. If the initial adsorption of this component before the area change was  $\Gamma_{k,\text{eq}}=N_{k,0}/A_0$ , in the moment  $t$  it will become

$$\Gamma_k(t) = \frac{N_{k,0} + \Delta N_k}{A_0 + \Delta A} \approx \Gamma_{k,\text{eq}}(1 - \alpha) + \frac{\Delta N_k}{A_0} \quad (1.9)$$

One sees that both effects, expansion and mass exchange, can be characterized by a single variable:

$$\varepsilon_k = -\frac{\tilde{\Gamma}_k}{\Gamma_{k,\text{eq}}} \approx \alpha - \frac{\Delta N_k}{\Gamma_{k,\text{eq}}A_0} = \alpha - \frac{\Delta N_k}{N_{k,0}} \quad (1.10)$$

where  $\tilde{\Gamma}_k = \Gamma_k - \Gamma_{k,\text{eq}}$ . The quantity  $\varepsilon_k$  is different from  $\alpha$  and has specific value for every component, whereas  $\alpha$  is the same for all components. For insoluble surfactants,  $\varepsilon_k = \alpha$ . We termed  $\varepsilon_k$  specific deformation (in [17,18] it was called “local deformation”), since it characterizes the area per molecule,  $a_k = 1/\Gamma_k$ , of each surfactant, as opposite to the total deformation,  $\alpha$ , which refers to the monolayer as a whole. One more advantage of  $\varepsilon_k$  as surface variable is that the surface pressure,  $\pi$ , at equilibrium or small deviation from it, is a function of the adsorption,  $\Gamma_k$ , or alternatively—of  $\varepsilon_k$ , rather than of  $\alpha$ . That  $\alpha$  is not appropriate as variable is obvious from the following example. Imagine that in a given moment the expansion  $\alpha$  in Eq. (1.10) is exactly compensated through diffusion by  $\Delta N_k/N_{k,0}$ , so that  $\tilde{\Gamma}_k = 0$ . Then

$$\tau_s = \pi_{\text{eq}} - \pi(\Gamma) = -E_G \frac{\tilde{\Gamma}}{\Gamma_{\text{eq}}} = E_G \varepsilon \quad (1.11)$$

which is proportional to  $\varepsilon$ , will be zero, although  $\alpha \neq 0$ . That is why Boussinesq [26] and Scriven [15] replaced in Voight equation the elastic stress by Eq. (1.11) and wrote (in our notations):

$$\tau_s(t) = E_G \varepsilon(t) + \eta_{\text{BS}} \dot{\alpha}(t) \quad (1.12)$$

where  $\eta_{\text{BS}}$  is the surface viscosity for this model.

We went further and argued in [17,18,27] that  $\dot{\alpha}$  in Eq. (1.12) must be also replaced by  $\dot{\varepsilon}$ . Our arguments were that no matter what the reason for the viscous stress is, it is always connected with the real surface concentrations  $\Gamma_k$  (i.e. with the specific variables  $\varepsilon_k$ ) since it is due to interactions between or transport of the adsorbed molecules. Hence, we proposed to define the stress in Voight model as (for a single component):

$$\tau_s(t) = E_G \varepsilon(t) + \eta_s \dot{\varepsilon}(t) \quad (1.13)$$

In fact, for soluble surfactants there is one more term due to the diffusion fluxes and proportional to  $\dot{\varepsilon}_k - \dot{\alpha}$  [see Eq. (3.30)], but as we will show in Section 4, it is also proportional to  $\varepsilon$ . In the present article we confirm and generalize this idea.

There are numerous methods for studying interfacial dynamics, described in several excellent books [16,28–31].

Based on the way the surface is perturbed, they can be classified in two groups:

- (i) Relaxational methods—they consist in suddenly expanding the area and following the subsequent relaxation of the surface pressure. The main methods use quick formation of a drop or bubble [32–37]. With some reservations the Bubble Pressure Method (BPM) falls also in this group. Since the main goal of these methods is the study of the kinetics of adsorption, they are now of less interest to us.
- (ii) The perturbational methods are based on continuous perturbation (expansion and/or contraction) of the interface. For insoluble surfactants this is usually done in a Langmuir trough by moving the barrier [38]. The most popular methods for soluble surfactants are the Oscillating Drop Method (ODM) [39–43] and its counterpart—the Oscillating Bubble Method (OBM) [44–52] using periodic oscillations of a drop or bubble. In our Expanding Drop Method (EDM) ([17,18], see also [53,54]) the drop is subject to continuous expansion or contraction with constant rate  $\dot{\alpha}$ . Other methods are the Overflowing Cylinder [30,55,56], using radial flow on a planar surface and the capillary waves method [14,57–63]. All methods in this group are based on following the response (by measuring the variation of the surface stress,  $\tau_s$ ) to the surface perturbation  $\alpha$  carried out with rate  $\dot{\alpha}$ , which gives the parameters of the used rheological constitutive equation.

All perturbational methods suffer to one degree or another of an important problem—the contribution of the shear surface viscosity to the surface stress, when such viscosity is present. The problem is that pure dilatation can be realized only with radial expansion of a perfect sphere. For all other deformations the total surface viscosity is a linear combination (with coefficients, depending on the geometry) of the dilatational and the shear viscosities (see e.g. [2,15,16]). The EDM and the version of ODM with spherical drop are the closest to using ideal sphere. The ODM, based on deformed pendant drop and its drop shape analysis is closer to a planar interface. This problem does not exist with non-interacting soluble surfactants, which exhibit only apparent surface viscosity, due to the mass transport to the surface (see Section 4.1). On the contrary, it can be very important for polymers and proteins or mixture of surfactants, exhibiting strong surface association and aggregation.

The theory of the interfacial rheology received much less attention. Presentation of the main theoretical concepts can be found in several books and review articles [15,16,64,65]. However, they are concerned mainly with application of the interfacial rheology to other phenomena, such as capillary wave damping or motion of drops or bubbles or to the interpretation of the data obtained with soluble surfactants.

There are several papers, studying the role of the interfacial curvature on the rheological equation [15,16], but in them too, the surface viscosities are merely constant parameters. With the notorious exception of the paper of Noskov [14], who attempted statistical mechanical calculations of the interfacial behavior of adsorbed polymers, we are not aware of a single mechanistic derivation of a rheological equation, involving true surface dilatational viscosity.

Our purpose was to fill this gap, at least in part, by deriving rheological equations for interacting insoluble and soluble surfactants, starting as much as possible from first principles. As a result we obtained also explicit expressions for the true and apparent surface viscosities [see Eqs. (2.24), (2.50), (2.54), (4.6) and (4.16)] in terms of the equilibrium values of the elasticities,  $E_k$ , and the areas per molecule,  $a_k$ , of the interacting compounds, the rate constant of the surface reaction and some other parameters in the case of soluble surfactants. Because of the very weak dependence of the interfacial tension on the radius of curvature, we neglected the latter in our equations, but it is tacitly assumed that the deformation is pure expansion or contraction. For information on the thermodynamics and kinetics of adsorption, which play important role in our theory, the reader is referred to the comprehensive book of Fainerman et al. [66].

In Section 2 we consider single surface reaction in a multi-component insoluble surfactant layer, subject to deformation  $\alpha$ . The reaction is described by means of the reaction coordinate  $\xi$  [67]. It is very important to realize that for any deformation  $\alpha$  there is an instantaneous quasi-equilibrium state characterized by a quasi-equilibrium value,  $\xi_{\text{eq}}$ , of  $\xi$ . The true chemical reaction takes place because of deviations from this state and is characterized by the relaxation part of the reaction coordinate:  $\xi_{\text{r}} = \xi - \xi_{\text{eq}}$ . In this way we derived a general rheological Eq. (2.24) giving as limiting cases Voight and Maxwell type equations. Expressions for all characteristics of the process: elasticity,  $E_A$ , reaction elasticity,  $E_r$ , reaction relaxation time,  $t_r$ , and true surface viscosity,  $\eta_s$ , are obtained [see the respective Eqs. (2.11), (2.21), (2.23), and (2.24)]. The results are analyzed for two specific types of deformation (constant rate of deformation,  $\dot{\alpha}$ , and periodic oscillations) and are applied to three simple surface reactions: monomolecular with one product, dimerization and association.

In Section 3 we treat simultaneously the processes of surface deformation, surface reaction and surfactant adsorption from the bulk. Since the mass of the surfactants is preserved during the reaction, but changes due to the adsorption, it turned out more convenient to formulate the equations in terms of the specific mass deformations,  $\varepsilon_k^s$  [see Eq. (3.13)], rather than in terms of  $\varepsilon_k$ . The obtained general rheological equation (3.30) contains only surface variables, but involves implicitly the surfactant fluxes,  $J_k$ , through the differences  $\dot{\varepsilon}_k^s - \dot{\alpha}$ . We showed however in Section 4, that at least under certain conditions  $J_k$  can be expressed through  $\varepsilon_k^s$ . In this way Eq. (3.30) became a

complete dynamic analog of Gibbs adsorption isotherm for a multi-component system under dynamic conditions with surface reaction—similarly to Gibbs equation it relates the surface stress only to surface variables (see also the Concluding remarks for more details). Generalizations of Voight and Maxwell equations for soluble surfactants were obtained as limiting cases and the general equation was again applied to two types of surface deformation and to three simple reactions.

Because of the complex coupling of surface reaction and mass transfer, in Section 4.1 we analyze first only the latter for a single component. In this system the surface stress is purely elastic, but we succeeded to show that if the surface perturbation,  $\tilde{I}$ , is small, regardless of the type of surface perturbation and the mechanism of adsorption, the process of mass transport always obeys a Maxwell type of rheological equation [see Eqs. (4.5) and (4.15)]. For all considered processes we defined surface viscosities as products of respective elasticity and characteristic time, analogously to the definition of  $\eta_s$  in Eq. (2.24). However, we called them “apparent surface viscosity”,  $\eta_s^{\text{app}}$ , because they stem from diffusion, rather than from interaction between the surfactant molecules, as  $\eta_s$  does. Besides, they depend also on the bulk parameter diffusivity,  $D$ , and on the geometry of the system, i.e. they are not typical surface property. We analyzed the relation of the “apparent film surface viscosity” [see Eq. (4.22)], which controls the drainage of thin liquid films and thereby—the lifetime of unstable emulsions and foams and the imaginary elasticity,  $G_i$ , defined by Lucassen and van den Tempel [68,69] and considered by some authors [70] as surface viscosity. We showed that the widely used correlations between  $G_i$  and the lifetime of emulsions and foams lack serious scientific foundations and can lead to erroneous conclusions. Even less foundations such correlations with  $G_i$  have in the case of equilibrium thin films and stable emulsions and foams. In Section 4.2 we analyzed the problem for the coupling of the surfactant diffusion with the chemical reaction and demonstrated on a simple example how it could be tackled.

In Section 5 we summarized and sometimes extended and generalized the conclusions we reached, based on the present theory.

## 2. Interfacial rheological models for insoluble surfactants

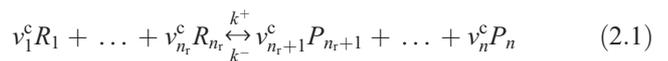
The simplest way for construction of rheological models for interfaces is to assume that the surface is an independent phase, which does not exchange adsorbed molecules with the surrounding bulk phases (insoluble surfactant model). We will model the chemical interactions between the adsorbed molecules by a single surface reaction. The respective rheological constitutive equation, derived in Section 2.1, contains the surface elasticity,  $E_A$ , the

relaxation time of the surface reaction,  $t_r$ , and the surface viscosity,  $\eta_s$ . For particular modes of surface deformation the reduction of the derived general surface-rheological equation to the constitutive laws of Voight and Maxwell is investigated in Section 2.2. The parameters of the general rheological model for some simple surface reactions (monomolecular, dimerization and surface association) are calculated in Section 2.3.

### 2.1. General surface rheological model for a single surface reaction

We will use throughout this article the following assumptions: (i) the adsorbed molecules in the monolayer are involved only in one surface chemical reaction; (ii) the deviations from equilibrium are so small, that all processes can be modeled as being linear; (iii) the surface pressure,  $\pi$ , depends only on the instantaneous values of the adsorptions,  $\Gamma_k(t)$ , i.e. all neglected relaxation processes at the surface have characteristic times much smaller than the characteristic times of the surface reaction, of the rate of surface deformation and of the bulk diffusion; and (iv) there is no mass transfer between the interface and the contiguous bulk phases for insoluble surfactants; (v) when soluble surfactants are present (as in Sections 3 and 4) for them assumption (iv) is replaced by the assumption for local equilibrium meaning that the adsorptions,  $\Gamma_k(t)$ , and the subsurface concentrations,  $c_{k,s}$ , are related through the equilibrium adsorption isotherm.

The number of reactants in the considered surface reaction is  $n_r$  and the reactants are denoted by  $R_1, \dots, R_{n_r}$ . The number of products is  $n_p$  and the number of all kind of molecules, taking part in the reaction, is  $n=n_r+n_p$ . The products are  $R_{n_r+1}, \dots, P_n$ . The surface reaction is illustrated with the following scheme:



where  $v_k^c$  ( $k=1, \dots, n$ ) are the stoichiometric coefficients,  $k^+$  is the rate constant of the forward reaction and  $k^-$  is the rate constant of the reverse reaction. In order to simplify the expressions, below algebraic stoichiometric coefficients are introduced:  $v_k \equiv -v_k^c$  ( $k=1, \dots, n_r$ ) and  $v_k \equiv v_k^c$  ( $k=n_r+1, \dots, n$ ). We will characterize the surface reaction by the reaction coordinate,  $\zeta_A$ , which is defined as [67]:

$$N_k - N_{k,0} = v_k \zeta_A \quad (k = 1, \dots, n) \quad (2.2)$$

where  $N_k$  and  $N_{k,0}$  are the number of molecules of the component  $k$  in the whole system at moment  $t$  and  $t=0$ , respectively. The reaction coordinate is a measure of the advancement of the chemical reaction at moment  $t$  with respect to the initial state at  $t=0$ . The rate of the reaction,  $v_A$ , is

$$v_A = \frac{1}{v_k} \frac{dN_k}{dt} = \frac{d\zeta_A}{dt} \quad (k = 1, \dots, n) \quad (2.3)$$

When the area,  $A$ , changes with time, the rate of change of the number of molecules of given kind per unit area (i.e. of the adsorption  $\Gamma_k \equiv N_k/A$ ) is given by:

$$\frac{d\Gamma_k}{dt} = \frac{d}{dt} \left( \frac{N_k}{A} \right) = \frac{1}{A} \frac{dN_k}{dt} - \frac{N_k}{A} \left( \frac{1}{A} \frac{dA}{dt} \right) \quad (k = 1, \dots, n) \quad (2.4)$$

or

$$\frac{1}{v_k} \left( \frac{d\Gamma_k}{dt} + \Gamma_k \dot{\alpha} \right) = \frac{1}{A} \frac{d\zeta_A}{dt} = \frac{v_A}{A} \quad (k = 1, \dots, n) \quad (2.5)$$

We assume that the surface deformation starts from immobile surface with equilibrium adsorptions,  $\Gamma_{k,eq}$ , at the initial moment,  $t=0$ . The adsorption,  $\Gamma_k$ , is presented as a sum of its equilibrium value,  $\Gamma_{k,eq}$ , and its perturbation  $\tilde{\Gamma}_k \equiv \Gamma_k - \Gamma_{k,eq}$ , where  $k=1, \dots, n$ . The initial values (at  $t=0$ ) of the perturbations of the adsorptions are zero, i.e.  $\tilde{\Gamma}_k(0)=0$ . Because we assumed small surface deformations [see assumption (ii)] we have  $\tilde{\Gamma}_k \ll \Gamma_{k,eq}$  and all equations can be linearized with respect to  $\dot{\alpha}$  and the perturbations  $\tilde{\Gamma}_k$ . Then Eq. (2.5) simplifies to:

$$\frac{1}{v_k} \left( \frac{d\tilde{\Gamma}_k}{dt} + \Gamma_{k,eq} \dot{\alpha} \right) = \frac{d\zeta}{dt} = v \quad (k = 1, \dots, n) \quad (2.6)$$

where the reaction coordinate  $\zeta$  and the rate of the chemical reaction per unit area are  $\zeta \equiv \zeta_A/A \approx \zeta_A/A_0$  and  $v \equiv v_A/A \approx v_A/A_0$ , respectively. The solutions of the differential Eq. (2.6) with initial conditions,  $\tilde{\Gamma}_k(0)=0$  and  $\zeta(0)=0$ , are:

$$\tilde{\Gamma}_k = -\Gamma_{k,eq} \alpha + v_k \zeta \quad (k = 1, \dots, n) \quad (2.7)$$

In order to find the reaction coordinate as a function of time, the dependence of  $v$  on the adsorptions,  $\Gamma_k$ , has to be known.

We will assume that the mechanism of the reaction corresponds exactly to the scheme, shown by Eq. (2.1). In real systems this is often not so, but in such cases the mechanism is represented by a set of parallel and/or consecutive reactions [71]. Dealing with such reactions is beyond the scope of the present theory. The total rate of the chemical reaction,  $v$ , is a difference between the rate of the forward reaction,  $v^+$ , and the rate of the reverse reaction,  $v^-$ . At equilibrium these rates are equal. For small perturbations the total rate,  $v$ , can be linearized with respect to the perturbations ( $\tilde{\Gamma}_k \ll \Gamma_{k,eq}$ ):

$$v = v^+ - v^- = k^+ \prod_{k=1}^{n_r} \Gamma_k^{v_k^+} - k^- \prod_{k=n_r+1}^n \Gamma_k^{v_k^-} \approx -v_{eq} \sum_{k=1}^n v_k \frac{\tilde{\Gamma}_k}{\Gamma_{k,eq}} \quad (2.8)$$

where  $v_{eq}$  is the rate of the forward or the reverse reactions at equilibrium:

$$v_{eq} \equiv k^+ \prod_{k=1}^{n_r} \Gamma_{k,eq}^{v_k^+} = k^- \prod_{k=n_r+1}^n \Gamma_{k,eq}^{v_k^-} \quad (2.9)$$

Finally, if the expressions for the perturbations in the adsorptions (2.7) are substituted into Eq. (2.8) one obtains the expression for the rate of the chemical reaction as a function of the surface deformation,  $\alpha$ , and the reaction coordinate,  $\zeta$ :

$$v = \frac{d\zeta}{dt} = v_{eq} v \alpha - \frac{\zeta}{t_r} \quad (2.10)$$

where the sum of all algebraic stoichiometric coefficients,  $v$ , the characteristic relaxation time of the surface reaction,  $t_r$ , and the area per adsorbed molecule of given kind at equilibrium,  $a_k$  ( $k=1, \dots, n$ ), are defined as:

$$v \equiv \sum_{k=1}^n v_k, \quad \frac{1}{t_r} \equiv v_{eq} \sum_{k=1}^n v_k^2 a_k, \quad a_k \equiv \frac{1}{\Gamma_{k,eq}} \quad (k = 1, \dots, n) \quad (2.11)$$

Before proceeding further we must account for the fact that during the surface deformation the equilibrium state of the system changes with the deformation. The total mass of the adsorbed molecules at the surface,  $M \equiv M_1 N_1 + \dots + M_n N_n$  ( $M_k$  is the molecular mass of the  $k$ -th component), remains constant during expansion/contraction (insoluble surfactants), but the total surface mass density of adsorbed molecules,  $A \equiv M/A$ , changes, due to the change of the area. Summing up all equations in Eq. (2.2), one finds that the total number of adsorbed molecules,  $N \equiv N_1 + \dots + N_n$ , is a function of their initial number,  $N_0$ , and the reaction coordinate:  $N = N_0 + v \zeta_A$ . The corresponding total adsorption,  $\Gamma \equiv N/A$ , is simply:  $\Gamma = (N_0 + v \zeta_A)/A$ . The total number of molecules,  $N$ , changes only due to the chemical reaction if  $v = v_1 + v_2 + \dots + v_n \neq 0$ . The total adsorption,  $\Gamma$ , changes even at  $v=0$  because of the change of the surface area.

This means that the equilibrium state shifts with  $\alpha$  (i.e. with time). Let us consider as example the reaction of dimerization—at equilibrium one has [cf. Eq. (2.9)]:

$$A_{eq} = M_1 \Gamma_{1,eq} + 2M_1 \Gamma_{2,eq} = M_1 \left( \Gamma_{1,eq} + 2 \frac{k^+}{k^-} \Gamma_{1,eq}^2 \right) \quad (2.12)$$

where  $\Gamma_{1,eq}$  and  $\Gamma_{2,eq}$  are the adsorptions of the monomers and the dimers at equilibrium. It is obvious from this equation that the change of the total surface mass density,  $A_{eq}$ , is accompanied by change of the equilibrium surface composition,  $\Gamma_{1,eq}$  and  $\Gamma_{2,eq}$ . If the surface deformation is quasi-static (infinitely slow) or the reaction infinitely fast, all the products of the reaction will be used to establish the new equilibrium state. The value of the reaction coordinate,  $\zeta$ , in this instantaneous equilibrium state, corresponding to a given value of  $\alpha$ , will be denoted by  $\zeta_{eq}(t)$ . Hence, the net production of the reaction, which we will denote by  $\zeta_r$  and will call relaxation of the reaction, must be defined with respect to  $\zeta_{eq}$  [rather than with respect to the initial value,

$\xi(0)=0$ ]. If the total production in the moment  $t$  is  $\xi$ , the net production will be

$$\xi_r = \xi - \xi_{\text{eq}} \quad (2.13)$$

As explained above, the equilibrium is achieved when the deformation rate is much smaller than the reaction rate. The reaction rate is characterized by the reaction relaxation time,  $t_r$  [see Eq. (2.11)]. The characteristic time of surface deformation, corresponding to  $\dot{\alpha}$ , will be  $t_{\text{def}} \approx \dot{\alpha}^{-1}$ . If one multiplies Eq. (2.10) by  $t_r$  and introduces a dimensionless time,  $t' \equiv t/t_{\text{def}}$ , the left hand side of Eq. (2.10) will become  $(t_r/t_{\text{def}}) (d\xi/dt')$ . Since at equilibrium,  $t_r/t_{\text{def}}=0$ , the derivative in Eq. (2.10) must vanish. Thus we obtain:

$$\xi_{\text{eq}} = v_{\text{eq}} t_r v \alpha \quad (2.14)$$

From Eqs. (2.7) and (2.14) the perturbations of the adsorptions,  $\tilde{\Gamma}_{k,\text{eq}}$  ( $k=1, \dots, n$ ), needed to maintain the equilibrium and the perturbations with respect to the quasi-equilibrium state  $\tilde{\Gamma}_{k,r}$  ( $k=1, \dots, n$ ), must be:

$$\begin{aligned} \tilde{\Gamma}_{k,\text{eq}} &= -\Gamma_{k,\text{eq}} \alpha + v_k \xi_{\text{eq}}, & \tilde{\Gamma}_{k,r} &\equiv \tilde{\Gamma}_k - \tilde{\Gamma}_{k,\text{eq}} \\ &= v_k \xi_r & (k=1, \dots, n) \end{aligned} \quad (2.15)$$

Substituting now  $\xi = \xi_{\text{eq}} + \xi_r$  into Eq. (2.10) and using the value of  $\xi_{\text{eq}}$  defined by Eq. (2.14), we find for  $\xi_r$  the differential equation of the reaction relaxation

$$\frac{d\xi_r}{dt} + \frac{\xi_r}{t_r} = -v_{\text{eq}} t_r v \dot{\alpha} \quad (2.16)$$

The two functions,  $\xi_{\text{eq}}$  and  $\xi_r$ , determine the instantaneous composition of the surface layer,  $\Gamma_k(t)$  ( $k=1, \dots, n$ ), and thereby—the surface pressure,  $\pi$ , and the surface stress,  $\tau_s$ . If the dependence of  $\pi$  on  $\Gamma_k(t)$  is described by the equilibrium equation of state [see assumption (iii)], the change of the surface pressure with respect to the initial state,  $\pi_{\text{eq}}$ , which corresponds to  $\Gamma_{k,\text{eq}}$ , will be (keeping only linear terms in the Taylor expansion):

$$\begin{aligned} \pi - \pi_{\text{eq}} &= \sum_{k=1}^n \left( \frac{\partial \pi}{\partial \Gamma_k} \right)_{\text{eq}} \tilde{\Gamma}_k = \sum_{k=1}^n a_k E_k \tilde{\Gamma}_k, \\ E_k &\equiv \left( \frac{\partial \pi}{\partial \ln \Gamma_k} \right)_{\text{eq}} \quad (k=1, \dots, n) \end{aligned} \quad (2.17)$$

where  $E_k$  is the partial Gibbs elasticity of the  $k$ -th component. If the solutions (2.15) for the perturbations  $\tilde{\Gamma}_k$  are substituted into Eq. (2.17), the change of the surface pressure, i.e. the surface stress,  $\tau_s$ , can be presented as a sum of three terms as follows:

$$\begin{aligned} -\tau_s = \pi - \pi_{\text{eq}} &= -\alpha \sum_{k=1}^n E_k + \xi_{\text{eq}} \sum_{k=1}^n v_k a_k E_k \\ &+ \xi_r \sum_{k=1}^n v_k a_k E_k \end{aligned} \quad (2.18)$$

The first term in the right hand side of Eq. (2.18) corresponds to the change of the surface pressure due only

to the change of the surface area. The second term therein stems from the shift of the equilibrium state, caused by the surface deformation. The third term is due to the relaxation of the surface reaction.

With Eq. (2.14) the second term in the right hand side of (2.18) can be transformed as follows:

$$\begin{aligned} \xi_{\text{eq}} \sum_{k=1}^n a_k v_k E_k &= \alpha v \sum_{k=1}^n v_k a_k E_k / \sum_{k=1}^n v_k^2 a_k \\ &= \alpha v \left( \sum_{k=n_r+1}^n v_k^c a_k E_k - \sum_{k=1}^n v_k^c a_k E_k \right) / \sum_{k=1}^n v_k^c a_k \end{aligned} \quad (2.19)$$

Eq. (2.19) shows that this term is proportional to the total surface deformation,  $\alpha$ , and the coefficient of proportionality is a weighted difference of the elasticities of the products and reactants of the surface reaction. For that reason we termed the coefficient of proportionality reaction elasticity,  $E_r$ :

$$E_r \equiv v \sum_{k=1}^n v_k a_k E_k / \sum_{k=1}^n v_k^2 a_k \quad (2.20)$$

The reaction elasticity reflects the change of the overall elasticity of the monolayer due to the transformation of part of the reactant molecules into molecules of the products. In the particular case of dilute surface layers,  $\pi = k_B T \Gamma$  ( $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature), and the following simple result holds:

$$E_r = k_B T v^2 / \sum_{k=1}^n v_k^2 a_k \geq 0 \quad (2.21)$$

Finally, the last term in Eq. (2.18) can be written as [cf. (2.20) and (2.11)]  $E_r \xi_r / (v_{\text{eq}} t_r v)$ . Then, Eq. (2.18) leads to the expression for the surface stress:

$$\tau_s = E_A \alpha - \frac{E_r}{v_{\text{eq}} t_r v} \xi_r \quad (2.22)$$

where the surface elasticity,  $E_A$ , is simply related to the partial Gibbs elasticities,  $E_k$  ( $k=1, \dots, n$ ), and the surface reaction elasticity,  $E_r$ :

$$E_A = \sum_{k=1}^n E_k - E_r \quad (2.23)$$

If the relaxation of the reaction coordinate,  $\xi_r$ , is substituted from Eq. (2.22) into Eq. (2.16), the following general rheological constitutive equation is obtained:

$$\frac{1}{E_r} (\dot{\tau}_s - E_A \dot{\alpha}) + \frac{1}{\eta_s} (\tau_s - E_A \alpha) = \dot{\alpha}, \quad \eta_s \equiv E_r t_r \quad (2.24)$$

where  $\eta_s$  is the surface dilatational viscosity. The mechanical scheme corresponding to Eq. (2.24) is illustrated in Fig. 1. It contains two elastic,  $E_A$  and  $E_r$ , and one viscous,

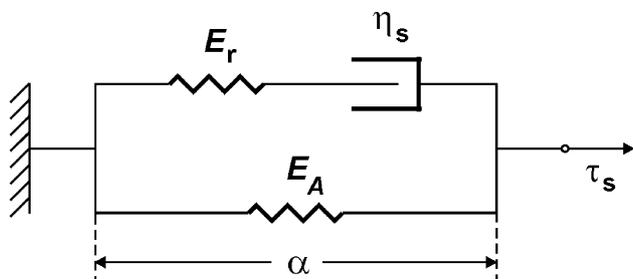


Fig. 1. Mechanical scheme of the rheological constitutive model (2.24).

$\eta_s$ , elements. We will often call  $\eta_s$  *true* surface viscosity to distinguish it from the apparent surface viscosity,  $\eta_s^{\text{app}}$ , defined in Section 4.1, which is due to the surfactant diffusion from the bulk. There are at least two reasons for using the adjective “true”:

- (i) This quantity originates only from the interactions between the surfactant molecules, which are at the surface, not in the bulk;
- (ii) It is defined only through surface properties [cf. Eq. (2.24) along with Eq. (2.11) and (2.20)] and therefore pertains only to the surface; moreover, its definition remains unchanged even for soluble surfactants (see Section 3.1).

This corresponds exactly to the Gibbs concept of treating the surface as separate phase even when it is not autonomous and can exchange matter with the contiguous bulk phases.

It follows from Eq. (2.20) that if  $v=0$ , i.e. if the total number of molecules does not change during the reaction, the reaction elasticity,  $E_r$ , and the surface viscosity,  $\eta_s$ , will be zero. This is true for any reaction in which the sums of the stoichiometric coefficients of the reactants and that of the products are equal. This conclusion is analogous to the well-known fact from chemical thermodynamics that for such systems the chemical equilibrium is not affected by the change of the size (volume or area) of the system [71]. Nevertheless, the reason for the validity of this result under dynamic conditions deserves a closer inspection, since the situation is different when soluble surfactants are involved in the reaction.

To understand the physical reason for this result, let us consider the case of simple molecular transformation when a single reactant  $R_1$  is transformed into a single product  $P_2$ . According to Eq. (2.7), during expansion (or contraction) the perturbations of the two adsorptions will be,  $\tilde{\Gamma}_k/\Gamma_{k,\text{eq}} = -\alpha + v_k \zeta/\Gamma_{k,\text{eq}}$  ( $k=1, 2$ ). However, they enter the reaction Eq. (2.8) with different signs ( $v_1=-1$  is negative and  $v_2=+1$  is positive) and since Eq. (2.8) is linear, the overall contribution of the term with  $\alpha$  is zero, since it is proportional to  $v_1+v_2=0$ . That is why for reactions with  $v=v_1+\dots+v_n=0$  the term with  $\alpha$  in Eq. (2.10) vanishes. The remaining term,  $-\zeta/t_r$ , in the right hand side of Eq. (2.10) cannot lead to shift in the equilibrium if the system

has been in equilibrium at  $t=0$ , since the solution of the respective equation for  $\zeta$  with  $\zeta(0)=0$ , is identically zero. Hence, the equilibrium state of a reaction of insoluble surfactants with  $v=0$  cannot be perturbed by expansion or contraction of the surface. However, we remind the reader that this conclusion results from the linearity of Eq. (2.8). The situation can be different if the rate of the reaction cannot be linearized.

## 2.2. Simplified rheological models for particular modes of surface deformation

The simplest way to find how Eq. (2.24) is connected with the Voight and Maxwell constitutive laws (1.4) and (1.5) is to consider oscillations of the surface with a given frequency,  $\omega$ . In this case all variables are proportional to  $\exp(i\omega t)$ , where  $i$  is the imaginary unit. The surface stress, following from Eq. (2.24), is:

$$\frac{\tau_s}{\alpha} = E_A + E_r \frac{\omega^2 t_r^2}{1 + \omega^2 t_r^2} + \frac{\eta_s}{1 + \omega^2 t_r^2} i\omega \quad (2.25)$$

For oscillations the Voight constitutive law (1.4) has the following form:

$$\frac{\tau_s}{\alpha} = E_V + \eta_V i\omega \quad (2.26)$$

In order to have the same form of Eqs. (2.25) and (2.26), their real and imaginary parts must be the same, i.e.

$$E_V = E_A + E_r \frac{\omega^2 t_r^2}{1 + \omega^2 t_r^2}, \quad \eta_V = \frac{\eta_s}{1 + \omega^2 t_r^2} \quad (2.27)$$

It is obvious that  $E_V$  will become independent of  $\omega$  only for  $\omega^2 t_r^2 \ll 1$ , i.e. for slow deformation (for low frequencies) or fast relaxation processes. If such is the case, the terms  $\omega^2 t_r^2$  in (2.27) can be neglected and the model (2.24) is reduced to the Voight constitutive equation with the following elasticity and dilatational surface viscosity:

$$E_V = E_A, \quad \eta_V = \eta_s \quad (2.28)$$

More complicated is the case with Maxwell model, which for oscillations leads to [see Eq. (1.5)]:

$$\frac{\tau_s}{\alpha} = \frac{\eta_M^2 E_M \omega^2}{E_M^2 + \omega^2 \eta_M^2} + \frac{\eta_M E_M^2}{E_M^2 + \omega^2 \eta_M^2} i\omega \quad (2.29)$$

This result can be put in a form similar to Eq. (2.25) if an appropriate relaxation time is introduced:  $t_M = \eta_M/E_M$ . Then the comparison of Eqs. (2.25) and (2.29) shows that they will be equivalent if

$$E_A + E_r \frac{\omega^2 t_r^2}{1 + \omega^2 t_r^2} = E_M \frac{\omega^2 t_M^2}{1 + \omega^2 t_M^2}, \quad \frac{\eta_s}{1 + \omega^2 t_r^2} = \frac{\eta_M}{1 + \omega^2 t_M^2} \quad (2.30)$$

The second Eq. (2.30) suggests that this is possible if  $\eta_M = \eta_s$  and  $t_M = t_r$ . Since  $\eta_s = t_r E_r$  and  $\eta_M = t_M E_M$ , this means also  $E_M = E_r$ . Then the first Eq. (2.30) implies  $E_A = 0$ .

The same conclusions follow directly from Eq. (2.24). If one scales the time by  $t_{\text{def}}$ , one sees that the first term in Eq. (2.24) is of the order of  $t_r/t_{\text{def}}$  and can be neglected for fast reaction or slow deformation. This leads to Voigt equation (more detailed analysis of this approximation is carried out in Section 4.2). Eq. (2.24) transforms into Maxwell Eq. (1.5) if one sets  $\eta_M = \eta_s$ ,  $E_M = E_r$  and  $E_A = 0$ . This result implies that the Maxwell model assumes compensation of the reaction elasticity,  $E_r$ , by the Gibbs' elasticities [see Eq. (2.23)] so that only the reaction surface elasticity,  $E_r$ , remains. This follows also from the general mechanical scheme in Fig. 1—if one disregards the element with elasticity  $E_A$ , it transforms into the familiar Maxwell scheme, but with elasticity  $E_r$ .

Another way to analyze Eq. (2.30) is to consider the case of slow relaxation (large  $t_r$  and  $t_M$ ) or high frequencies, when the square terms in the denominators in Eq. (2.30) become large. Then the conditions for their equivalency [up to the second order in the small parameter  $1/(\omega^2 t_r^2) \ll 1$ ] will be:

$$E_M = E_A + E_r, \quad \eta_M = \eta_s \left( 1 + \frac{E_A}{E_r} \right)^2 \quad (2.31)$$

The second simple and important process is a continuous expansion/contraction with a constant rate of surface deformation,  $\dot{\alpha}$ . Then the rheological Eq. (2.24) has a simple solution (with  $\tau_s = 0$  at  $t = 0$ ):

$$\tau_s = E_A \alpha + \eta_s [1 - \exp(-t/t_r)] \dot{\alpha} \quad (2.32)$$

At short times ( $t \ll t_r$ ) it corresponds to purely elastic behavior but with elasticity  $E_A + E_r = E_1 + \dots + E_n$  [cf. Eq. (2.23)]. At  $t \gg t_r$  it leads to a Voigt type equation. If one introduces in Eq. (2.32) the deformation time,  $t_{\text{def}} = \dot{\alpha}^{-1}$ , and the dimensionless time,  $t' = t/t_{\text{def}}$ ,  $t/t_r$  becomes  $t'(t_{\text{def}}/t_r)$  and one sees again that the short time limit corresponds to fast deformation ( $t_{\text{def}} \ll t_r$ ) and the long time limit—to slow deformation ( $t_{\text{def}} \gg t_r$ ).

It is instructive to look at the behavior of  $\xi_{\text{eq}}$ ,  $\xi$  and  $\xi_r$  for the case of continuous deformation. The expressions for  $\xi$  and  $\xi_r$  are obtained by solving Eqs. (2.10) and (2.16) with initial conditions  $\xi = \xi_r = 0$  at  $t = 0$ . The results can be written as:

$$\begin{aligned} \frac{\xi_{\text{eq}}}{v_{\text{eq}} t_r v} &= \frac{t}{t_{\text{def}}}, & \frac{\xi_r}{v_{\text{eq}} t_r v} &= -\frac{t_r}{t_{\text{def}}} [1 - \exp(-t/t_r)], \\ \frac{\xi_r}{v_{\text{eq}} t_r v} &\approx -\frac{t_r}{t_{\text{def}}} \quad (\text{at } t \gg t_r) \end{aligned} \quad (2.33)$$

$$\begin{aligned} \frac{\xi}{v_{\text{eq}} t_r v} &= \frac{t}{t_{\text{def}}} - \frac{t_r}{t_{\text{def}}} [1 - \exp(-t/t_r)], \\ \frac{\xi}{v_{\text{eq}} t_r v} &\approx \frac{t - t_r}{t_{\text{def}}} \quad (\text{at } t \gg t_r) \end{aligned} \quad (2.34)$$

The functions  $\xi_{\text{eq}}$ ,  $\xi$  and  $\xi_r$  are plotted in Fig. 2 for  $t_r/t_{\text{def}} = 0.5$ . Note that their signs depend on the change of the

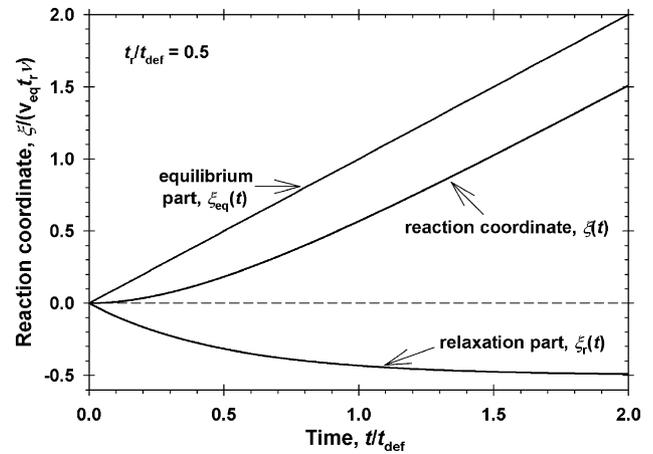


Fig. 2. Dependence of the dimensionless reaction coordinates,  $\xi/(v_{\text{eq}} t_r v)$ ,  $\xi_{\text{eq}}/(v_{\text{eq}} t_r v)$  and  $\xi_r/(v_{\text{eq}} t_r v)$ , on the dimensionless time,  $t/t_{\text{def}}$ , at  $t_r/t_{\text{def}} = 0.5$ .

number of molecules involved in the reaction,  $v$ , see Eqs. (2.33) and (2.34)). The dimensionless relaxation,  $\xi_r/(v_{\text{eq}} t_r v)$ , has always opposite sign to  $\xi/(v_{\text{eq}} t_r v)$  and  $\xi_{\text{eq}}/(v_{\text{eq}} t_r v)$ . Originally, at  $t \ll t_r$ ,  $\xi_r$  is approximately equal to  $\xi_{\text{eq}}$  (with opposite sign). At  $t \gg t_r$ , it reaches a constant value, i.e. the rate  $d\xi_r/dt$  becomes zero. In this time range  $\xi$  is parallel to  $\xi_{\text{eq}}$ , but shifted at a distance  $t_r/t_{\text{def}}$ , see Eqs. (2.33) and (2.34). This means that at  $t \gg t_r$  a steady state is established and all products of the reaction are consumed only for maintaining the quasi-equilibrium state, which is continuously shifting with  $\alpha$ , i.e. with time. However, the system can never reach the quasi-equilibrium state. The limiting deviation from the equilibrium,  $\xi_r(\infty) = -v_{\text{eq}} v t_r^2 / t_{\text{def}}$ , depends on  $t_r$  and  $t_{\text{def}}$ —it is large for slow reactions and fast expansions.

For long time  $t$  or fast relaxation processes, when  $t \gg t_r$ , the exponent in Eq. (2.32) can be neglected and the Voigt constitutive law with parameters (2.27) is recovered. The Voigt model has an important shortcoming—at moment  $t = 0$ , when  $\alpha = 0$ , the stress is not zero, but  $\eta \sqrt{\dot{\alpha}}$ . This “initial jump” is due to the unrealistic assumption that the constant deformation rate,  $\dot{\alpha}$ , is established instantly. In reality, every apparatus will have some acceleration period,  $t_{\text{app}}$ , before it reaches constant deformation rate. This problem can be avoided even in the framework of the Voigt model, by taking a more realistic function  $\dot{\alpha}(t)$ , accounting for the acceleration period, e.g.

$$\dot{\alpha}(t) = \dot{\alpha}_\infty [1 - \exp(-t/t_{\text{app}})] \quad (2.35)$$

which is zero at  $t = 0$  and increases to the constant rate  $\dot{\alpha}_\infty$  at  $t \gg t_{\text{app}}$ . This problem does not exist for the general model (2.32).

For a constant rate of surface deformation the Maxwell constitutive Eq. (1.5) has the following solution [20]:

$$\tau_s = \eta_M [1 - \exp(-t/t_M)] \dot{\alpha} \quad (2.36)$$

At short times ( $t \ll t_M$ ) it corresponds to purely elastic behavior with elasticity  $E_M$ , i.e. again it assumes  $E_A = 0$ . At

$t \gg t_r$  the Maxwell model leads to purely viscous behavior:  $\tau_s = \eta_M \dot{\alpha}$ . For slow relaxation processes ( $t_r \gg t$ ) the exponential term in Eq. (2.32) can be expanded in series up to second order in  $t/t_r$ . Then the expression for the surface stress becomes:

$$\tau_s \approx (E_A + E_r)\alpha - \frac{\eta_s}{2t_r^2} t^2 \dot{\alpha} + \dots \quad (2.37)$$

The corresponding second order approximation for the Maxwell model (2.36) is found to be:

$$\tau_s \approx E_M \alpha - \frac{\eta_M}{2t_M^2} t^2 \dot{\alpha} + \dots \quad (2.38)$$

By applying the same reasoning as when we obtained (2.31), one finds again that the expressions (2.37) and (2.38) will be equivalent if the parameters of the Maxwell constitutive law obey the relationships (2.31).

The above conclusions for the validity of Voight and Maxwell models can be confirmed for arbitrary rate of surface deformation. The solution of Eq. (2.24) is presented in integral form as:

$$\tau_s = E_A \alpha + \frac{\eta_s}{t_r} \int_0^t \exp\left(\frac{\tilde{t}-t}{t_r}\right) \ddot{\alpha}(\tilde{t}) d\tilde{t} \quad (2.39)$$

After two subsequent partial integrations of the integral in Eq. (2.39) one obtains:

$$\begin{aligned} \tau_s = & E_A \alpha + \eta_s \{ [\dot{\alpha}(t) - t_r \ddot{\alpha}(t)] - [\dot{\alpha}(0) - t_r \ddot{\alpha}(0)] \exp(-t/t_r) \} \\ & + \eta_s t_r \int_0^t \exp\left(\frac{\tilde{t}-t}{t_r}\right) \ddot{\alpha}(\tilde{t}) d\tilde{t} \end{aligned}$$

where  $\ddot{\alpha}$  and  $\ddot{\alpha}$  are the second and third derivatives of the surface deformation function,  $\alpha$ , with respect to time, respectively. Eqs. (2.39) and (2.40) show that after each step of the partial integration new terms, proportional to  $\exp(-t/t_r)$ , appear in the series. If  $t/t_r \gg 1$ , these terms will disappear. The situation with the second term on the right hand side of Eq. (2.40), containing  $\dot{\alpha}$  and  $t_r \ddot{\alpha}$ , is more complicated. However, if one assumes a reasonable dependence of  $\alpha$  on  $t$ , say like this in Eq. (2.35), one has  $\dot{\alpha} \approx \dot{\alpha}_\infty$  and  $t_r \ddot{\alpha} \approx \dot{\alpha}_\infty (t_r/t_{app})$ . Then, for  $t_r \ll t_{app}$ , the term with  $\ddot{\alpha}$  can be neglected and the leading order terms in the series (2.40) will give the Voight constitutive law with the parameters defined by Eq. (2.28).

In the opposite case, of  $t \ll t_r$ , the exponential term in the general solution (2.39) can be linearized to yield:

$$\tau_s = \left( E_A + \frac{\eta_s}{t_r} \right) \alpha + \frac{\eta_s}{t_r^2} \int_0^t (\tilde{t}-t) \dot{\alpha}(\tilde{t}) d\tilde{t} \quad (2.41)$$

The Maxwell Eq. (1.5) for an arbitrary rate of surface deformation has the following integral form:

$$\tau_s = E_M \int_0^t \exp[-(\tilde{t}-t)/t_M] \dot{\alpha}(\tilde{t}) d\tilde{t} \quad (2.42)$$

For slow relaxation processes Eq. (2.42) is simplified to:

$$\tau_s = E_M \alpha + \frac{\eta_M}{t_M^2} \int_0^t (\tilde{t}-t) \dot{\alpha}(\tilde{t}) d\tilde{t} \quad (2.43)$$

Therefore, the rheological model (2.24) is reduced again to the Maxwell constitutive law with the parameters defined through Eq. (2.31) for fast surface deformations.

### 2.3. Simple surface reactions

Below three particular cases of surface reactions are considered. The simplest one is a single reactant,  $R_1$ , which is transformed into a single product,  $P_2$ :



The stoichiometric coefficients are:

$$v_1^c = -v_1 = v_2^c = v_2 = 1, \quad v = 0 \quad (2.45)$$

From Eqs. (2.9) and (2.11) the equilibrium rate and the relaxation time of the reaction are:

$$v_{eq} = k^+ \Gamma_{1,eq} = k^- \Gamma_{2,eq}, \quad \frac{1}{t_r} = k^+ + k^- \quad (2.46)$$

Since,  $v=0$ , the definitions (2.20) and (2.24) show that the reaction elasticity,  $E_r$ , and the surface viscosity,  $\eta_s$ , are zero. Actually, they will be zero not only for a monomolecular reaction, but for any reaction for which  $v=0$ , i.e. for which the total number of molecules does not change. However, this is true only for insoluble surfactants—if the surfactants are soluble, even these reactions exhibit viscous behavior, but it is due to the energy dissipation, accompanying the adsorption/desorption processes (see Section 3.3).

The general scheme of a surface dimerization reaction is:



The stoichiometric coefficients are:

$$v_1^c = -v_1 = 2, \quad v_2^c = v_2 = 1, \quad v = -1 \quad (2.48)$$

From Eqs. (2.9) and (2.11) the equilibrium rate and the relaxation time of the reaction are:

$$v_{eq} = k^+ \Gamma_{1,eq}^2 = k^- \Gamma_{2,eq}, \quad t_r = \frac{1}{k^-} \frac{a_2}{4a_1 + a_2} \quad (2.49)$$

From the definitions (2.20) and (2.24) and Eq. (2.49) the reaction elasticity,  $E_r$ , and the surface dilatational viscosity,  $\eta_s$ , are:

$$E_r = \frac{2a_1 E_1 - a_2 E_2}{4a_1 + a_2}, \quad \eta_s = \frac{E_r a_2}{k^- (4a_1 + a_2)} \quad (2.50)$$

The dimerization is the first step toward formation of larger two-dimensional “drops” and a surface phase transition, exhibited by many surfactants with long hydrocarbon tails. The effect of this process on the interfacial

dynamics was studied in [28,30] but from a different viewpoint. If however, there is no formation of chemical (or at least hydrogen) bonds between the molecules, the van der Waals interaction between the tails is too weak to hold firmly the molecules together, so that the dissociation rate constant,  $k^-$ , is very large and the surface viscosity is very low—our estimates showed that the latter is well below the resolution power of any method we are aware of.

The third example is surface association:



with stoichiometric coefficients:

$$v_1^c = -v_1 = v_2^c = -v_2 = v_3^c = v_3 = 1, \quad v = -1 \quad (2.52)$$

From Eqs. (2.9) and (2.11) the equilibrium rate and the relaxation time of the reaction (2.51) are found to be:

$$v_{\text{eq}} = k^+ \Gamma_{1,\text{eq}} \Gamma_{2,\text{eq}} = k^- \Gamma_{3,\text{eq}}, \quad t_r = \frac{1}{k^-} \frac{a_3}{a_1 + a_2 + a_3} \quad (2.53)$$

From the definitions (2.20) and (2.24) and Eq. (2.53) the reaction elasticity,  $E_r$ , and the surface dilatational viscosity,  $\eta_s$ , become:

$$E_r = \frac{a_1 E_1 + a_2 E_2 - a_3 E_3}{a_1 + a_2 + a_3}, \quad \eta_s = \frac{E_r a_3}{k^- (a_1 + a_2 + a_3)} \quad (2.54)$$

### 3. Role of the bulk diffusion on the interfacial rheological model

In Section 2 the surface was described as an autonomous phase, which does not exchange molecules with the contiguous bulk phases. As it was mentioned in the Introduction, for soluble surfactants the specific and the total surface deformations are different. This difference is due to the bulk diffusion fluxes, which modify the adsorptions,  $\Gamma_k$ , with respect to what they would have been if the only external perturbation (with respect to the surface) were the change of total area. In this section we will consider only the modification of the surface constitutive Eq. (2.24), involved by the bulk diffusion fluxes,  $J_k$ . However, since the solution of the diffusion problem has some peculiarities, we postpone the derivation of explicit expressions for the fluxes to Section 4 where we will show also, how they are coupled with the rheological equation.

In Section 3.1 the rheological model for a single surface reaction, Eq. (2.24), is extended for soluble surfactants by taking into account the role of the bulk diffusion fluxes. It is shown that, because of the difference between the specific and total surface deformations, new surface viscosity coefficients appear. The extended rheological model is reduced under certain conditions to generalized Voight and Maxwell models (see Section 3.2). The coefficients of the

rheological equation for simple surface reactions are calculated in Section 3.3.

#### 3.1. General rheological model for soluble surfactants

We consider in this section a surface mixture of insoluble and soluble surfactants. Assumptions (i), (ii), (iii) and (iv) from Section 2.1 will be used again for insoluble surfactants—assumption (iv) is replaced by (v) when considering soluble surfactants. The total number of the soluble components is  $j$ , their indexes in the series of reactants and products in Eq. (2.1) are  $1 \leq k_1, \dots, k_j \leq n$  and the soluble surfactants have bulk concentrations  $c_{k_1}, \dots, c_{k_j}$ . The other reactants and/or products of the reaction appear only at the surface, i.e. they cannot adsorb from or desorb to the bulk solution.

To make the role of the surface reaction evident, we will carry out the presentation in two steps: (i) static experiments and (ii) dynamic experiments. First the situation without reaction will be considered and then the effects of the surface reaction will be shown.

##### 3.1.1. Static experiments

We begin by presenting some basic well-known equations for a system of  $n$  soluble surfactants without chemical reaction between them. The static experiments with this system consist in measuring the equilibrium surface pressure,  $\pi_{\text{eq}}$ , as a function of the equilibrium bulk concentrations of the surfactants,  $c_{1,\text{eq}}, \dots, c_{n,\text{eq}}$ . The Gibbs equation, written for constant temperature,  $T$ , relates the change of the surface pressure to the adsorptions,  $\Gamma_k$ , and the change of the surface chemical potentials,  $\mu_k^s$  ( $k=1, \dots, n$ ), of the components [38]:

$$d\pi = \sum_{k=1}^n \Gamma_k d\mu_k^s \quad (3.1)$$

At equilibrium the surface chemical potentials of the species are equal to the respective bulk chemical potentials, so that:

$$d\pi_{\text{eq}} = k_B T \sum_{k=1}^n \Gamma_{k,\text{eq}} d(\ln c_{k,\text{eq}}) \quad (3.2)$$

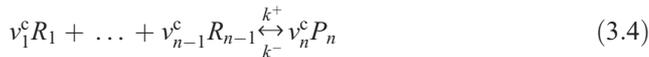
By means of Eq. (3.2) the experimentalist can calculate the adsorptions at equilibrium by varying only one concentration, say  $c_{k,\text{eq}}$ , and measuring the resulting variation of  $\pi_{\text{eq}}$ :

$$\Gamma_{k,\text{eq}} = \frac{1}{k_B T} \frac{\partial \pi_{\text{eq}}}{\partial (\ln c_{k,\text{eq}})} \quad (k = 1, \dots, n) \quad (3.3)$$

Eqs. (3.2) and (3.3) allow experimental determination of the equilibrium surface pressure isotherm,  $\pi_{\text{eq}} = \pi_{\text{eq}}(c_{1,\text{eq}}, \dots, c_{n,\text{eq}})$ , and the adsorption isotherms,  $\Gamma_{k,\text{eq}} = \Gamma_{k,\text{eq}}(c_{1,\text{eq}}, \dots, c_{n,\text{eq}}; k=1, \dots, n)$ .

With surface chemical reaction at equilibrium the chemical potentials,  $\mu_k^s$ , are no longer independent. To make the treatment more transparent, let us assume that the

reactants,  $R_1, \dots, R_{n-1}$ , are soluble and the only product of the reaction,  $P_n$ , is insoluble. This surface reaction is illustrated with the scheme:



The condition for surface chemical equilibrium requires

$$v_1^c \mu_1^s + \dots + v_{n-1}^c \mu_{n-1}^s = v_n^c \mu_n^s \quad (3.5)$$

Substituting  $\mu_n^s$  from Eq. (3.5) into Eq. (3.1) and taking into account the fact that at equilibrium the surface chemical potential of a given soluble surfactant is equal to the respective bulk chemical potential, we obtain:

$$d\pi_{\text{eq}} = k_B T \sum_{k=1}^{n-1} \left( \Gamma_{k,\text{eq}} + \frac{v_k^c}{v_n^c} \Gamma_{n,\text{eq}} \right) d(\text{ln}c_{k,\text{eq}}) \quad (3.6)$$

If the experimentalist does not suspect the existence of a chemical reaction, he/she will think that the result, obtained from the measurements of  $\pi_{\text{eq}}$  vs.  $c_{k,\text{eq}}$ , is  $\Gamma_{k,\text{eq}}$ , but in fact it is:

$$\frac{1}{k_B T} \frac{\partial \pi_{\text{eq}}}{\partial (\text{ln}c_{k,\text{eq}})} = \Gamma_{k,\text{eq}} + \frac{v_k^c}{v_n^c} \Gamma_{n,\text{eq}} \quad (k = 1, \dots, n-1) \quad (3.7)$$

For the monomolecular reaction (2.44) the right hand side of Eq. (3.7) is  $\Gamma_{1,\text{eq}} + \Gamma_{2,\text{eq}}$ , for the surface dimerization (2.47) it is  $\Gamma_{1,\text{eq}} + 2\Gamma_{2,\text{eq}}$  and for the surface association (2.51), where there are two soluble reactants, 1 and 2, and one insoluble product, 3, there will be two results for the total adsorptions:  $\Gamma_{1,\text{eq}} + \Gamma_{3,\text{eq}}$  and  $\Gamma_{2,\text{eq}} + \Gamma_{3,\text{eq}}$ . Therefore, for the reaction under consideration the experimentalist obtains from the derivative of  $\pi_{\text{eq}}$  vs.  $\text{ln}c_{k,\text{eq}}$  not the individual adsorption  $\Gamma_{k,\text{eq}}$  of the component  $k$ , but the total adsorption of the component  $k$  regardless of under what form it is on the surface.

Multiplying and dividing each term in the right hand side of Eq. (3.6) by the molecular mass,  $M_k$ , the equation can be rewritten in a more general form:

$$d\pi_{\text{eq}} = k_B T \sum_{k=k_1}^{k_j} \frac{A_{k,\text{eq}}}{M_k} d(\text{ln}c_{k,\text{eq}}) \quad (3.8)$$

where  $A_{k,\text{eq}}$  ( $k=k_1, \dots, k_j$ ) is the equilibrium value of the total surface mass density,  $A_k$ , of the soluble component  $k$  including all its forms at the surface (reactants and products). The concept of “surface mass density” is more general, since it is applicable also to reactions of exchange. The specific connection between  $A_k$  and the adsorptions  $\Gamma_k$  for such reactions depends on the type of reaction and can be rather complicated. We will not enter here into these details. The surface mass densities at equilibrium (not the adsorptions) can be calculated from static experiments, by applying Eq. (3.8):

$$A_{k,\text{eq}} = \frac{M_k}{k_B T} \frac{\partial \pi_{\text{eq}}}{\partial (\text{ln}c_{k,\text{eq}})} \quad (k = k_1, \dots, k_j) \quad (3.9)$$

Eqs. (3.8) and (3.9) allow one to obtain the experimental equilibrium isotherms for  $\pi_{\text{eq}}$  and  $A_{k,\text{eq}}$  as functions of the composition of the solution:  $\pi_{k,\text{eq}} = \pi_{k,\text{eq}}(c_{k_1,\text{eq}}, \dots, c_{k_j,\text{eq}})$  and  $A_{k,\text{eq}} = A_{k,\text{eq}}(c_{k_1,\text{eq}}, \dots, c_{k_j,\text{eq}})$  ( $k=k_1, \dots, k_j$ ). Therefore, the surface elasticity,  $E_k^s$ , of the soluble component  $k$ , calculated from static experiments with surface reaction, is equal to:

$$E_k^s \equiv \left( \frac{\partial \pi}{\partial \text{ln}A_k} \right)_{\text{eq}} = A_{k,\text{eq}} \sum_{i=k_1}^{k_j} \left( \frac{\partial \pi}{\partial c_i} \right)_{\text{eq}} \left( \frac{\partial c_i}{\partial A_k} \right)_{\text{eq}} \quad (k = k_1, \dots, k_j) \quad (3.10)$$

### 3.1.2. Dynamic experiments

Even without surface reaction the surface pressure,  $\pi$ , is no longer function only of the concentrations, but also of the surface deformation,  $\alpha$ , and the rate of surface deformation,  $\dot{\alpha}$ . We will assume again, that the surface pressure is determined only by the instantaneous values of the adsorptions of all components,  $\Gamma_k(t)$  [see assumption (iii) in Section 2.1]. This means that we can use the equilibrium equation of state and the only effect of the time dependent factors (surface deformation,  $\alpha$ , and bulk diffusion fluxes,  $J_k$ ) is to change  $\Gamma_k(t)$ . Then for small deviation from a given equilibrium state, with adsorptions  $\Gamma_{k,\text{eq}}$  ( $k=1, \dots, n$ ), the Taylor expansion of the surface equation of state gives:

$$\begin{aligned} \pi &\approx \pi_{\text{eq}} + \sum_{k=1}^n \left( \frac{\partial \pi}{\partial \text{ln}\Gamma_k} \right)_{\text{eq}} \frac{\Gamma_k - \Gamma_{k,\text{eq}}}{\Gamma_{k,\text{eq}}} \\ &= \pi_{\text{eq}} + \sum_{k=1}^n E_k \frac{\Gamma_k - \Gamma_{k,\text{eq}}}{\Gamma_{k,\text{eq}}} \end{aligned} \quad (3.11)$$

where the coefficients of the expansion (3.11) are the partial Gibbs elasticities,  $E_k$  [for their definition see Eq. (2.17)]. This result is a generalized elastic law [see Eq. (1.10)] for a multi-component system of soluble surfactants:

$$\begin{aligned} \tau_s &= \pi_{\text{eq}} - \pi = \sum_{k=1}^n E_k \varepsilon_k, \quad \varepsilon_k = \frac{\Gamma_{k,\text{eq}} - \Gamma_k}{\Gamma_{k,\text{eq}}} \\ (k &= 1, \dots, n) \end{aligned} \quad (3.12)$$

where the relative perturbations of the adsorptions,  $\varepsilon_k$ , are termed specific deformations. The value of the partial Gibbs elasticity,  $E_k$ , appearing in Eq. (3.12), is supposed to be known or at least it can be calculated from static experiments, i.e. by means of Eqs. (3.2) and (3.3), for systems without surface reactions. In Section 4.1 we will derive a rheological constitutive equation for soluble surfactants without reaction under dynamic conditions.

We turn now to our final goal—dynamic experiments with soluble surfactants with surface reaction. When the data for such system are processed in terms of the surfactant bulk concentrations, the surface elasticities,  $E_k^s$ , and the surface mass densities,  $A_k$ , must be used instead of the partial Gibbs elasticities,  $E_k$ , and the adsorptions,  $\Gamma_k$ . Accordingly, the specific deformations must refer to  $A_k$ , rather than to  $\Gamma_k$  as

in Eq. (3.12). Hence, we introduce the specific mass deformations:

$$\varepsilon_k^s \equiv \frac{A_{k,\text{eq}} - A_k}{A_{k,\text{eq}}} \quad (k = k_1, \dots, k_j) \quad (3.13)$$

The bulk diffusion fluxes,  $J_k$  ( $k=k_1, \dots, k_j$ ), must be also introduced into the mass balance Eq. (2.6) for the perturbations of the adsorptions of the soluble components. Then, instead of Eq. (2.6) one has for any individual soluble surfactant

$$\frac{1}{v_k} \left( \frac{d\tilde{\Gamma}_k}{dt} + \Gamma_{k,\text{eq}} \dot{\alpha} + J_k \right) = \frac{d\zeta}{dt} = v \quad (k = k_1, \dots, k_j) \quad (3.14)$$

where  $\tilde{\Gamma}_k$  is the total perturbation of the adsorption  $\Gamma_k(t)$ , due to all perturbing factors: the flux from the bulk, the surface reaction and the surface deformation. The corresponding mass balance equations for the insoluble surfactants, Eq. (2.6), do not change. On the other hand, since the total mass of a given component is conserved during the chemical reaction and can change only due to the diffusion from the bulk, the surface mass densities,  $A_k$ , of the soluble components do not change with the advancement of the surface chemical reaction—they change only because of the change of the surface area and of the bulk diffusion fluxes. Hence, the perturbations of the surface mass density of the soluble component  $k$ , i.e.  $\tilde{A}_k(t) = A_k(t) - A_{k,\text{eq}}$ , obey equations, following from Eq. (3.14), with  $v=0$ :

$$\frac{d\tilde{A}_k}{dt} + A_{k,\text{eq}} \dot{\alpha} + M_k J_k = 0 \quad (k = k_1, \dots, k_j) \quad (3.15)$$

From the definition (3.13) and the mass balance Eq. (3.15) the bulk diffusion flux,  $J_k$ , can be expressed through the difference between the rate of specific mass deformation,  $\dot{\varepsilon}_k^s$ , and the rate of total surface deformation,  $\dot{\alpha}$ :

$$J_k = \frac{A_{k,\text{eq}}}{M_k} (\dot{\varepsilon}_k^s - \dot{\alpha}) \quad (k = k_1, \dots, k_j) \quad (3.16)$$

Eliminating the bulk diffusion flux,  $J_k$ , by subtracting Eq. (3.15) from Eq. (3.14), we obtain:

$$\frac{1}{v_k} \left[ \frac{1}{dt} \left( \tilde{\Gamma}_k - \frac{\tilde{A}_k}{M_k} \right) + \left( \Gamma_{k,\text{eq}} - \frac{A_{k,\text{eq}}}{M_k} \right) \dot{\alpha} \right] = \frac{d\zeta}{dt} = v \quad (k = k_1, \dots, k_j) \quad (3.17)$$

The solution of the differential Eq. (3.17) with initial conditions,  $\Gamma_k(0)=0$ ,  $\tilde{A}_k(0)=0$  and  $\zeta(0)=0$ , is

$$\tilde{\Gamma}_k - \frac{\tilde{A}_k}{M_k} = - \left( \Gamma_{k,\text{eq}} - \frac{A_{k,\text{eq}}}{M_k} \right) \alpha + v_k \zeta \quad (k = k_1, \dots, k_j) \quad (3.18)$$

The respective perturbations of the adsorptions of the insoluble surfactants are calculated from Eq. (2.7) as it is done in Section 2.1. Note that the mass balance Eq. (3.17) and

its solution (3.18) are analogs of Eqs. (2.6) and (2.7), derived for insoluble surfactants. The difference is that, because of the diffusion, the total perturbations of the adsorption of the soluble components,  $\tilde{\Gamma}_k$  (due both to the surface deformation and the reaction), in Eqs. (2.6) and (2.7) are replaced now with the difference,  $\tilde{\Gamma}_k - \tilde{A}_k/M_k$ , between the total perturbations of the adsorptions,  $\tilde{\Gamma}_k$ , and the perturbations of the surface mass density,  $\tilde{A}_k/M_k$ , due to the diffusion.

In order to derive the relaxation equation for the reaction coordinate, the solutions (2.7) for the insoluble surfactants and the solutions (3.18) for the soluble surfactants, along with the definition of the specific mass deformations (3.13), are substituted into the linearized expression for the total rate of the surface reaction (2.8). The result reads:

$$v = \frac{d\zeta}{dt} = v_{\text{eq}} v \alpha - \frac{\zeta}{t_r} + v_{\text{eq}} \sum_{k=k_1}^{k_j} \frac{v_k A_{k,\text{eq}}}{M_k \Gamma_{k,\text{eq}}} (\varepsilon_k^s - \alpha) \quad (3.19)$$

where the relaxation time,  $t_r$ , is defined by Eq. (2.11). The relaxation Eq. (3.19) is the counterpart of Eq. (2.10). Eq. (3.19) transforms into Eq. (2.10) for insoluble surfactants, for which the specific mass deformations,  $\varepsilon_k^s$ , are equal to the total surface deformation,  $\alpha$ . The quasi-equilibrium reaction coordinate,  $\zeta_{\text{eq}}$ , is defined analogously to Section 2.1, i.e. by setting the rate of the surface reaction,  $v$ , equal to zero:

$$\zeta_{\text{eq}} = v_{\text{eq}} t_r v \alpha + v_{\text{eq}} t_r \sum_{k=k_1}^{k_j} \frac{v_k A_{k,\text{eq}}}{M_k \Gamma_{k,\text{eq}}} (\varepsilon_k^s - \alpha) \quad (3.20)$$

As one could expect, the quasi-equilibrium state depends not only on the total deformation,  $\alpha$ , (as it is for insoluble surfactants), but also on the specific mass deformations [compare Eq. (3.20) with Eq. (2.14)]. The relaxation with respect to the quasi-equilibrium state,  $\zeta_r$ , is defined as a difference between the instantaneous value of the reaction coordinate,  $\zeta$ , and its quasi-equilibrium value,  $\zeta_{\text{eq}}$ , see Eq. (2.13). Using Eq. (3.20) and the relaxation Eq. (3.19) the following relation between  $\zeta_{\text{eq}}$  and  $\zeta_r$  is obtained:

$$\frac{d\zeta_r}{dt} + \frac{\zeta_r}{t_r} = - \frac{d\zeta_{\text{eq}}}{dt} \quad (3.21)$$

It shows that the only reason for the relaxation  $\zeta_r$  of the reaction is the change of the quasi-equilibrium state, no matter what the driving forces for this change are. By substituting Eq. (3.20) into (3.21) and expressing therein the result  $\dot{\varepsilon}_k^s - \dot{\alpha}$  through the fluxes  $J_k$  by means of Eq. (3.16), we obtain the following differential equation for  $\zeta_r$ :

$$\frac{d\zeta_r}{dt} + \frac{\zeta_r}{t_r} = - v_{\text{eq}} t_r v \dot{\alpha} - v_{\text{eq}} t_r \sum_{k=k_1}^{k_j} v_k a_k J_k \quad (3.22)$$

The two terms in the right hand side are the driving factors of the relaxation process: the first one accounts for the change of area of the adsorbed layer in the moment  $t$  and the second one—for the change of the total number of molecules of all soluble components in the same moment. A better insight of these processes can be gained from the following consid-

erations. The total area can be presented as  $A=N_k a_k=N_k/\Gamma_k$ , so that, if  $N_k$  is constant,  $\dot{\alpha}:=d \ln A/dt=-\left(\partial \ln \Gamma_k/\partial t\right)_{N_k}$ . On the other side, in the second term in the right hand side of Eq. (3.22) one can substitute  $a_k J_k=-a_k\left(\partial A_k/\partial t\right)_{\alpha} / M_k$ . Finally, since  $\nu=\nu_1+\dots+\nu_n$ , Eq. (3.22) acquires the form:

$$\frac{d \zeta_r}{d t}+\frac{\zeta_r}{t_r}=\nu_{\text {eq}} t_r\left[\sum_{k=1}^n \nu_k\left(\frac{\partial \ln \Gamma_k}{\partial t}\right)_{N_k}+\sum_{k=k_1}^{k_j} \nu_k \frac{a_k}{M_k}\left(\frac{\partial A_k}{\partial t}\right)_{\alpha}\right] \quad (3.23)$$

Therefore, the term with  $\dot{\alpha}$  [the first term in the right hand side of Eq. (3.23)] describes the change of adsorption due to the surface deformation at constant number of adsorbed molecules,  $N_k$ , while the second one describes the change of  $N_k$  due to mass transport from the bulk of the solution at constant area.

Everything said at the end of Section 2.1 about the role of  $\nu=\nu_1+\dots+\nu_n$  will be valid in the present case too. However, since the term with the fluxes  $J_k$  in Eq. (3.22) involves only some of the components, namely, the soluble surfactants, it will not vanish even when  $\nu=0$ , since part of the terms in the sum in Eq. (3.23) will be missing. Hence, it can perturb the quasi-equilibrium and lead to surface relaxation and energy dissipation even when  $\nu=0$ —then the reaction elasticity,  $E_r$ , and the surface viscosity,  $\eta_s$ , defined in Eqs. (2.20) and (2.24) will still be zero (because they are proportional to  $\nu$ ), but new diffusional viscosities appears, which are due to the fluxes,  $J_k$  (see below). This situation is illustrated in Section 3.3 on the example of a monomolecular reaction.

From Eqs. (3.19)–(3.21) the differential equation for  $\zeta_r$  is obtained:

$$\frac{d \zeta_r}{d t}+\frac{\zeta_r}{t_r}=-\nu_{\text {eq}} t_r \nu \sum_{k=k_1}^{k_j} \nu_k^s \dot{\epsilon}_k^s-\nu_{\text {eq}} t_r\left(\nu_s-\nu\right) \sum_{k=k_1}^{k_j} \nu_k^s\left(\dot{\epsilon}_k^s-\dot{\alpha}\right) \quad (3.24)$$

where the weighted stoichiometric coefficients, corresponding to the soluble species,  $\nu_k^s$  ( $k=k_1, \dots, k_j$ ) and  $\nu_s$ , are defined through the relationships:

$$\nu_s \equiv \sum_{k=k_1}^{k_j} \frac{\nu_k A_{k, \text {eq}}}{M_k \Gamma_{k, \text {eq}}}, \quad \nu_k^s \equiv \frac{\nu_k A_{k, \text {eq}}}{\nu_s M_k \Gamma_{k, \text {eq}}} \quad (k=k_1, \dots, k_j) \quad (3.25)$$

Applying Eq. (3.18) to the quasi-equilibrium state we obtain the quasi-equilibrium values of the perturbations of the adsorptions of the soluble species,  $\tilde{\Gamma}_{k, \text {eq}}$  and the perturbations with respect to the quasi-equilibrium state,  $\tilde{\Gamma}_k$ :

$$\tilde{\Gamma}_{k, \text {eq}}=\frac{\tilde{A}_k}{M_k}-\left(\Gamma_{k, \text {eq}}-\frac{A_{k, \text {eq}}}{M_k}\right) \alpha+\nu_k \zeta_{\text {eq}}, \quad \tilde{\Gamma}_k=\tilde{\Gamma}_{k, \text {eq}}+\nu_k \zeta_r \quad (k=k_1, \dots, k_j) \quad (3.26)$$

For the perturbations of the adsorptions of the insoluble species Eq. (2.15) is used, but with the quasi-equilibrium

and relaxation reaction coordinates,  $\zeta_{\text {eq}}$  and  $\zeta_r$  respectively, given by Eq. (3.20) and (3.24).

We will assume again that the two-dimensional surface pressure,  $\pi$ , depends explicitly only on the values of the adsorptions [assumption (iii) in Section 2.1]. Since the relaxations of all adsorptions,  $\Gamma_k$ , with respect to their values in the quasi-equilibrium state,  $\Gamma_{k, \text {eq}}+\tilde{\Gamma}_{k, \text {eq}}$ , depend on a single relaxation coordinate,  $\zeta_r$ , one has  $\pi=\pi\left(\Gamma_1, \Gamma_2, \dots, \Gamma_n\right)=\pi\left(\Gamma_{1, \text {eq}}+\tilde{\Gamma}_{1, \text {eq}}, \dots, \Gamma_{n, \text {eq}}+\tilde{\Gamma}_{n, \text {eq}} ; \zeta_r\right)$ . For  $\zeta_r=0$ , the dependence  $\pi\left(\Gamma_{1, \text {eq}}+\tilde{\Gamma}_{1, \text {eq}}, \dots, \Gamma_{n, \text {eq}}+\tilde{\Gamma}_{n, \text {eq}} ; 0\right)$  coincides with the experimental equilibrium isotherm. The expression for the surface stress is derived by expanding  $\tau_s$  in series of  $\epsilon_k^s$  and  $\zeta_r$  in the same way as Eq. (2.22) was obtained [see Eqs. (2.17)–(2.22)]:

$$\tau_s=\sum_{k=k_1}^{k_j} E_k^s \epsilon_k^s-\frac{E_r}{\nu_{\text {eq}} t_r \nu} \zeta_r \quad (3.27)$$

where the surface elasticities,  $E_k^s$ , are defined by Eq. (3.10). The first term in the right hand side of Eq. (3.27) seems different from the respective term  $E_A \alpha$  in Eq. (2.22) [cf. also Eq. (2.23)]. The difference is due to the fact that the summation in Eq. (3.27) is carried out only over soluble components whereas in Eq. (2.23) it is over all  $n$  insoluble components. If in Eq. (3.27) one sets  $\epsilon_k^s=\alpha$  (insoluble surfactants) and uses the relations (3.18) between  $\epsilon_k^s$  and  $\epsilon_k$ , and Eqs. (3.9) and (3.10)—between  $E_k^s$  and  $E_k$ , after some algebra one can show that the sum in Eq. (3.27) is transformed for insoluble surfactants into  $\left(E_1+\dots+E_n-E_r\right) \alpha$ .

After substituting Eq. (3.27) into the relaxation Eq. (3.22) one obtains the rheological equation:

$$t_r\left(\dot{\tau}_s-\sum_{k=k_1}^{k_r} E_k^s \dot{\epsilon}_k^s\right)+\left(\tau_s-\sum_{k=k_1}^{k_r} E_k^s \epsilon_k^s\right)=E_r t_r \dot{\alpha}+\frac{\eta_s}{\nu} \sum_{k=k_1}^{k_j} \nu_k a_k J_k \quad (3.28)$$

Another form of Eq. (3.28) is obtained if the diffusion fluxes,  $J_k$ , are substituted from Eq. (3.16) into Eq. (3.27):

$$t_r\left(\dot{\tau}_s-\sum_{k=k_1}^{k_r} E_k^s \dot{\epsilon}_k^s\right)+\left(\tau_s-\sum_{k=k_1}^{k_r} E_k^s \epsilon_k^s\right)=\eta_s \dot{\alpha}+\frac{\eta_s}{\nu} \sum_{k=k_1}^{k_j} \frac{\nu_k A_{k, \text {eq}}}{M_k \Gamma_{k, \text {eq}}}\left(\dot{\epsilon}_k^s-\dot{\alpha}\right) \quad (3.29)$$

After rearranging the terms in Eq. (3.29) it can be written also as:

$$t_r\left(\dot{\tau}_s-\sum_{k=k_1}^{k_j} E_k^s \dot{\epsilon}_k^s\right)+\left(\tau_s-\sum_{k=k_1}^{k_j} E_k^s \epsilon_k^s\right)=\eta_s \sum_{k=k_1}^{k_j} \nu_k^s \dot{\epsilon}_k^s+\sum_{k=k_1}^{k_j} \eta_k^{\text {diff}}\left(\dot{\epsilon}_k^s-\dot{\alpha}\right) \quad (3.30)$$

In Eq. (3.30) the new quantities  $\eta_k^{\text{diff}}$  ( $k=k_1, \dots, k_j$ ) are defined as:

$$\eta_k^{\text{diff}} \equiv \eta_s \left( \frac{v_s}{v} - 1 \right) v_k^s, \quad (k = k_1, \dots, k_j) \quad (3.31)$$

They multiply the differences  $\dot{\epsilon}_k^s - \dot{\alpha}$ , which are proportional to the diffusion fluxes,  $J_k$  [see Eq. (3.16)]. Therefore, they account for the energy dissipation in the surface reaction due to the molecules adsorbed through diffusion in the moment  $t$ . For this reason we termed  $\eta_k^{\text{diff}}$  diffusional dilatational interfacial viscosity. The difference between  $\eta_s$  and  $\eta_k^{\text{diff}}$  is determined by the different way of taking part in the reaction by the reactants molecules, that were at the surface in the moment  $t$  and were experiencing only the extension of the surface and those, which arrived at the surface at this very moment  $t$ . These two types of molecules correspond to the two terms in the right hand side of Eq. (3.23) respectively. The former not only react, but are also produced by the products in the reverse reaction. The latter only react and for them in the initial moment  $t$  the products seem to be absent. That is why their contribution to  $\eta_s$  is different. This is reflected in the respective relaxation times. From the viewpoint of the newly arrived molecules the adsorption of the products is effectively zero, which corresponds for them to infinite area per molecule. Indeed, if in  $t_r$  in Eq. (2.49) one assumes  $a_2 \gg a_1$  one obtains  $t_r = 1/k^-$ , which is exactly the relaxation time in Eq. (3.37) below. The same can be shown for the reaction of association.

It is noteworthy that the rheological Eq. (3.30) is formulated only in terms of the surface variables,  $\tau_s$ ,  $\epsilon_s$  and  $\dot{\alpha}$ , and all coefficients are physicochemical properties of the surface and do not depend explicitly on time, diffusion coefficients or geometry of the system. As already argued, it is a counterpart for a dynamic system, containing soluble surfactants with surface reaction, to the Gibbs isotherm (3.1), written in terms of the surface chemical potentials,  $\mu_k^s$ . The next step, which will be done in Section 4, of explicitly accounting of the exchange of matter with the contiguous bulk phases, is equivalent to replacing in Eq. (3.1)  $\mu_k^s$  by the bulk chemical potentials,  $\mu_k^b$ , and using the respective expressions for  $\mu_k^b$  in terms of the bulk concentrations,  $c_k$ . The surface elasticities,  $E_{k_1}^s, \dots, E_{k_j}^s$  in Eq. (3.30) correspond to the equilibrium state and they can be considered as known parameters, which can be calculated from independent equilibrium measurements. The obtained rheological model transforms into that for insoluble surfactants, Eq. (2.24), if the following substitutions are made:  $\alpha = \epsilon_{k_1}^s, \dots, = \epsilon_{k_j}^s$  and  $E_A = E_{k_1}^s, \dots, + E_{k_j}^s$ .

### 3.2. Generalized Voight and Maxwell equations for soluble surfactants

We showed in Section 2, that the general surface rheological model (2.24) for insoluble surfactants is reduced under certain conditions to the Voight or to the Maxwell constitutive laws. In the case of soluble surfactants these

constitutive equations must be modified, by taking into account the difference between the surface deformation,  $\alpha$ , and the specific mass deformations,  $\epsilon_k^s$ . This can be done directly from the general Eq. (3.30) as we did in Section 2.2 for Eq. (2.24). After introducing in Eq. (3.30) the dimensionless time  $t' = t/t_{\text{def}}$  one sees that the first term in the left hand side is of the order of  $t_r/t_{\text{def}}$  and is negligible for fast reaction or slow deformation (see also Section 4.2 for details). If such is the case, one obtains a generalized form of Voight equation for soluble surfactants:

$$\tau_s = \sum_{k=k_1}^{k_j} E_k^s \dot{\epsilon}_k^s + \eta_s \sum_{k=k_1}^{k_j} v_k^s \dot{\epsilon}_k^s + \sum_{k=k_1}^{k_j} \eta_k^{\text{diff}} (\dot{\epsilon}_k^s - \dot{\alpha}) \quad (3.32)$$

The second and the third terms in the right hand side are counterpart of the term  $\eta_s \dot{\alpha}$  in Voight equation for insoluble surfactants. As shown above, they both have the meaning of driving force for the surface reaction in the process under consideration—the second term accounts for the role of the surface deformation and is analogous to  $\eta_s \dot{\alpha}$  for insoluble surfactants, but the third term, containing the sum over  $\dot{\epsilon}_k^s - \dot{\alpha}$ , is entirely due to the mass transport from the bulk and has no counterpart for insoluble surfactants. The second and the third term in the right hand side of Eq. (3.32) can be replaced by the right hand side of any of the Eqs. (3.28) and (3.29). For the particular case of surface conformational change, Eq. (3.32) was derived previously by us in [27] by means of the non-equilibrium thermodynamics.

Another way for deriving Voight equation is by solving the differential Eq. (3.30) to obtain:

$$\tau_s = \sum_{k=k_1}^{k_j} E_k^s \dot{\epsilon}_k^s + \frac{1}{t_r} \int_0^t \exp\left(\frac{\tilde{t}-t}{t_r}\right) \left[ \eta_s \sum_{k=k_1}^{k_j} v_k^s \dot{\epsilon}_k^s + \sum_{k=k_1}^{k_j} \eta_k^{\text{diff}} (\dot{\epsilon}_k^s - \dot{\alpha}) \right] d\tilde{t} \quad (3.33)$$

which is the counterpart for soluble surfactants of Eq. (2.39). Following an analogous way to that in Section 2.2 (for arbitrary rate of surface deformation) after partial integration of Eq. (3.33) with respect to the exponential term the following result is derived:

$$\tau_s \approx \sum_{k=k_1}^{k_j} E_k^s \dot{\epsilon}_k^s + \eta_s \left[ \sum_{k=k_1}^{k_j} v_k^s \dot{\epsilon}_k^s(t) - \sum_{k=k_1}^{k_j} v_k^s \dot{\epsilon}_k^s(0) \exp(-t/t_r) \right] + \sum_{k=k_1}^{k_j} \eta_k^{\text{diff}} \left\{ [\dot{\epsilon}_k^s(t) - \dot{\alpha}(t)] - [\dot{\epsilon}_k^s(0) - \dot{\alpha}(0)] \exp(-t/t_r) \right\} \quad (3.34)$$

The rheological model (3.34) has no “jump” of the surface stress at initial time  $t=0$ . If one neglects the exponential terms in Eq. (3.34), it is transformed into the Voight type Eq. (3.32).

A Maxwell type equation can be obtained from the general Eq. (3.30) by simply neglecting (as it was done in Section 2.2) in the left hand side the terms  $\sum E_k^s \dot{\epsilon}_k^s$  and

$\Sigma E_k^s \dot{\varepsilon}_k^s$ , i.e. by assuming that all surface elasticities,  $E_k^s$ , are zero. Then:

$$t_r \dot{\tau}_s + \tau_s = \eta_s \sum_{k=k_1}^{k_j} v_k^s \dot{\varepsilon}_k^s + \sum_{k=k_1}^{k_j} \eta_k^{\text{diff}} (\dot{\varepsilon}_k^s - \dot{\alpha}) \quad (3.35)$$

Again the right hand side of Eq. (3.35) can be replaced by any right hand side of Eqs. (3.28) and (3.29).

### 3.3. Simple surface reactions

We will calculate here only  $\eta_k^{\text{diff}}$ , because it is the only new parameter, appearing in Eq. (3.30) with respect to Eq. (2.24). The relaxation time,  $t_r$ , and the surface viscosity,  $\eta_s$ , are defined in Section 2.1, see Eqs. (2.11) and (2.24).

For one reactant,  $R_1$ , which is transformed into one product,  $P_2$ , the model reaction and the corresponding parameters are given by Eqs. (2.44)–(2.47) in Section 2.3. In the considered case of soluble surfactants, only  $\varepsilon_1^s$  appears in Eq. (3.30), which is simplified to:

$$t_r (\dot{\tau}_s - E_1^s \dot{\varepsilon}_1^s) + (\tau_s - E_1^s \varepsilon_1^s) = \eta_1^{\text{diff}} (\dot{\varepsilon}_1^s - \dot{\alpha}),$$

$$\eta_1^{\text{diff}} = \frac{1}{k^+ + k^-} \frac{a_1 E_1 - a_2 E_2}{a_2} \quad (3.36)$$

The rheological model (3.36) is visco-elastic, whereas if both components  $R_1$  and  $P_2$  are insoluble, it is purely elastic (Section 2.3)—this difference is due to the diffusion, leading to the appearance of the diffusional surface viscosity,  $\eta_1^{\text{diff}}$ . If the two components form an ideal surface layer,  $\pi = k_B T (\Gamma_1 + \Gamma_2)$  and  $\eta_1^{\text{diff}} = 0$ .

In the case of dimerization, see Eq. (2.47), and soluble reactants, again only  $\varepsilon_1^s$  appears. For definition of the parameters see Eqs. (2.48)–(2.50) in Section 2.3. From Eq. (3.30) the respective rheological constitutive law becomes:

$$t_r (\dot{\tau}_s - E_1^s \dot{\varepsilon}_1^s) + (\tau_s - E_1^s \varepsilon_1^s) = \eta_s \dot{\varepsilon}_1^s + \eta_1^{\text{diff}} (\dot{\varepsilon}_1^s - \dot{\alpha}),$$

$$\eta_1^{\text{diff}} = \eta_s \frac{4a_1 + a_2}{a_2} = \frac{E_r}{k^-} \quad (3.37)$$

For this process  $\eta_1^{\text{diff}}$  is never zero (if  $\eta_s$  is finite), no matter what the surface equation of state is.

In the case of association of soluble reactants with insoluble product [see Section 2.3 and definitions therein, Eqs. (2.51)–(2.54)] two specific deformations appear:  $\varepsilon_1^s$  and  $\varepsilon_2^s$ . For that reason the model (3.30) is more complicated:

$$t_r (\dot{\tau}_s - E_1^s \dot{\varepsilon}_1^s - E_2^s \dot{\varepsilon}_2^s) + (\tau_s - E_1^s \varepsilon_1^s - E_2^s \varepsilon_2^s)$$

$$= \eta_s (v_1^s \dot{\varepsilon}_1^s + v_2^s \dot{\varepsilon}_2^s) + \eta_1^{\text{diff}} (\dot{\varepsilon}_1^s - \dot{\alpha}) + \eta_2^{\text{diff}} (\dot{\varepsilon}_2^s - \dot{\alpha}) \quad (3.38)$$

The diffusional surface viscosity,  $\eta_1^{\text{diff}}$  and  $\eta_2^{\text{diff}}$ , and the weighted stoichiometric coefficients, calculated for this reaction from Eqs. (3.25) and (3.31) are:

$$v_1^s = \frac{a_1 + a_3}{a_1 + a_2 + 2a_3}, \quad v_2^s = \frac{a_2 + a_3}{a_1 + a_2 + 2a_3} \quad (3.39)$$

$$\eta_1^{\text{diff}} = v_1^s \frac{E_r}{k^-}, \quad \eta_2^{\text{diff}} = v_2^s \frac{E_r}{k^-} \quad (3.40)$$

For this process the diffusional surface viscosities are different from zero only if the reaction elasticity,  $E_r$ , and thus— $\eta_s$ , is different from zero.

## 4. True and apparent surface viscosities in dynamic experiments

In this section we will generalize the rheological equation for soluble surfactants (3.30), derived in Section 3, in order to describe the phenomena observed in real experiments with soluble surfactants, mainly at constant rate of surface deformation,  $\dot{\alpha}$ , or with periodic perturbation of the surface with angular velocity,  $\omega$ . As already mentioned, the surface stress is affected by the diffusion fluxes, which not only change the adsorptions and thus modify the specific deformations,  $\varepsilon_k$ , and  $\varepsilon_k^s$ , but lead also to the appearance of the diffusional surface viscosity,  $\eta_s^{\text{diff}}$  (see Section 3). Since the diffusion is a dissipative process, it leads also to the appearance of a dissipative term in the surface stress even in the absence of surface reaction—we will call this effect apparent surface viscosity,  $\eta_s^{\text{app}}$ , for reasons to become clear later.

When a chemical reaction takes place at the surface, the effect of the apparent surface viscosity,  $\eta_s^{\text{app}}$ , is coupled with that of the true surface viscosity,  $\eta_s$ , which complicates the analysis of the rheological data. Reasonably simple expressions for  $\tau_s$  can be derived at the expense of some approximations, which depend on the mechanism of the reaction, on the adsorption isotherm, as well as on the range of variation of the experimental conditions: concentrations,  $\alpha$  and  $\dot{\alpha}$  or  $\omega$ . Hence, we will not attempt a general solution for this case, but in Section 4.2 we will demonstrate with a simple example how the problem can be tackled.

We will confine ourselves to the case of one soluble surfactant, when the rheological model (3.30) is simplified to:

$$t_r (\dot{\tau}_s - E_s \dot{\varepsilon}_s) + (\tau_s - E_s \varepsilon_s) = \eta_s \dot{\varepsilon}_s + \eta_s^{\text{diff}} (\dot{\varepsilon}_s - \dot{\alpha}) \quad (4.1)$$

For the sake of simplicity the subscript “1” is omitted, i.e. the surface elasticity,  $E_1^s$ , and the specific mass deformation,  $\varepsilon_1^s$ , are denoted as  $E_s$  and  $\varepsilon_s$ , respectively. The diffusion problem for soluble surfactants without reaction will be solved separately in Section 4.1 before the discussion of the respective rheological equations. In Section 4.2 we will demonstrate how the diffusion problem is coupled with the rheological constitutive law (4.1).

#### 4.1. Deformation of a purely elastic surface-apparent surface viscosity

In this section we will investigate the simplest case of a purely elastic deformation, which is realized when there is no chemical reaction at the surface. Hence, the Gibbs elasticity,  $E_G$ , and the surface elasticity,  $E_s$ , are equal; so are also the specific deformations,  $\varepsilon$  and  $\varepsilon_s$  [see Eqs. (3.12) and (3.13)].

##### 4.1.1. Surfactant diffusion toward small spherical drops with constant rate of deformation

We consider first the case of slow diffusion (which is assumed now to be the rate-determining process for the transport of the soluble surfactant) to the surface of a small spherical drop with initial radius,  $R_0$ . The drop is subject to small uniform expansion or contraction with rate of surface deformation,  $\dot{\alpha}$ , and the surfactant solution is placed outside the drop. The advantage of this geometry is that under certain conditions (see below) it leads to steady state solution of the diffusion equation. The bulk diffusion equation for perturbations of the concentration,  $\tilde{c}$ , must be solved in spherical coordinate system with radial coordinate,  $r$ :

$$\frac{\partial \tilde{c}}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \tilde{c}}{\partial r} \right) \quad \text{at } r \geq R_0 \quad (4.2)$$

where  $D$  is the surfactant diffusivity. The initial perturbations (at  $t=0$ ) of the concentration and the adsorption are assumed zero. In the case of diffusion-controlled processes we assume local adsorption equilibrium, which means that the subsurface concentration,  $c_s(t)$ , is connected to the instantaneous adsorption,  $\Gamma(t)$ , through the equilibrium adsorption isotherm—this is one boundary condition for the problem (4.2); for the perturbation of the adsorption,  $\tilde{\Gamma}$ , and the subsurface concentrations,  $\tilde{c}_s$ , it yields  $\tilde{\Gamma} = h_a \tilde{c}_s$ , where the adsorption length,  $h_a$ , is defined as  $h_a = (\partial \Gamma / \partial c)_{\text{eq}}$  [7]. The mass balance equation for the perturbation of the adsorption,  $\tilde{\Gamma}$ , due to the bulk diffusion,  $J$ , and to the rate of surface deformation,  $\dot{\alpha}$ , gives the second boundary condition. For small perturbations it is:

$$\frac{d\tilde{\Gamma}}{dt} + \Gamma_{\text{eq}} \dot{\alpha} = -J = D \frac{\partial \tilde{c}}{\partial r} \quad \text{at } r = R_0 \quad (4.3)$$

We consider small drops or large adsorption lengths, i.e. we assume  $R_0 \ll h_a$ . The radial coordinate can be scaled with the drop radius,  $R_0$ , and the time scale can be chosen to be  $t_{\text{dr}} = h_a R_0 / D$ . After writing Eqs. (4.2) and (4.3) in dimensionless form, a parameter, which we assume small,  $R_0 / h_a \ll 1$ , appears only before the time derivative of the concentration in Eq. (4.2). The solution of Eq. (4.2) with the boundary condition  $\tilde{c} = \tilde{c}_s$  at  $r = R_0$  yields  $\tilde{c} = \tilde{c}_s R_0 / r$ . Substituting  $\tilde{c}_s = \tilde{\Gamma} / h_a$  we find that the leading term of the solution of Eq. (4.2) is  $\tilde{c} = (R_0 \tilde{\Gamma}) / (h_a r)$ . The same solution is obtained if the time is scaled with the characteristic time of the

deformation,  $t_{\text{def}} = \dot{\alpha}^{-1}$ , and the assumption for slow surface deformation is used, i.e. if  $R_0^2 / (t_{\text{def}} D) \ll 1$ . If the obtained solution for  $\tilde{c}$  is used to calculate  $\partial \tilde{c} / \partial r$  in the boundary condition (4.3), the following differential equation is derived:

$$\frac{d\tilde{\Gamma}}{dt} + \Gamma_{\text{eq}} \dot{\alpha} = -\frac{\tilde{\Gamma}}{t_{\text{dr}}} \quad (4.4)$$

For purely elastic surface deformation the surface stress is  $\tau_s = E_G \varepsilon$ . The specific deformation is defined as  $\varepsilon = -\tilde{\Gamma} / \Gamma_{\text{eq}}$ . By eliminating  $\varepsilon$  from these two expressions and substituting the result for  $\tilde{\Gamma}$  in Eq. (4.4), the following constitutive equation is obtained:

$$\frac{1}{E_G} \dot{\tau}_s + \frac{1}{E_G t_{\text{dr}}} \tau_s = \dot{\alpha} \quad (4.5)$$

Eq. (4.5) is exactly the Maxwell constitutive law (1.5) with elasticity  $E_M = E_G$  and surface viscosity  $\eta_M = E_G t_{\text{dr}}$ . The second term in the left hand side of Eq. (4.5) stems from the bulk diffusion, i.e. the dissipation of energy, due to the diffusion, leads to the appearance of a viscous term in the rheological equation. The fact that this process is described by Maxwell equation corresponds to its nature. The overall process of surface extension and mass transfer consists of two stages: a dissipative (viscous) diffusional stage, followed by an elastic stage—surface deformation without reaction. This exactly corresponds to Maxwell model (see the Introduction)—a viscous and an elastic element connected in series. The viscosity term in Eq. (4.5) is different from the true surface viscosity,  $\eta_s$ , and for that reason we will call the product

$$\eta_s^{\text{app}} = E_G t_{\text{dr}} = E_G h_a R_0 / D \quad (4.6)$$

“apparent surface viscosity”. Analogously to  $\eta_s$  in Eq. (2.24), the apparent surface viscosity, defined above, is equal to the product of elasticity and characteristic time.

One of the reasons to call  $\eta_s^{\text{app}}$  “apparent” is the fact that the surface stress is purely elastic (see above), but due to the diffusion the interface behaves as though there is also a surface viscous stress. Moreover, the apparent surface viscosity is not a physicochemical property of the interface because of its dependence on bulk parameters and the system geometry (in this example on the drop radius,  $R_0$ , and the bulk diffusion coefficient,  $D$ ). One more reason to claim that  $\eta_s^{\text{app}}$  is not a true interfacial properties is that it does not fit into Gibbs concept of the interface as a separate phase, which is described only by quantities pertaining to the interface, such as  $\tau_s$ ,  $E_k$ ,  $\varepsilon_k$ ,  $\alpha$  and  $\eta_s$  (see Sections 2 and 3). Finally,  $\eta_s^{\text{app}}$  does not stem from interactions between the adsorbed molecules, as the true surface viscosity,  $\eta_s$ , does.

In order to investigate the range of validity of the steady-state solution of Eq. (4.2) we solved exactly the diffusion problem (4.2)–(4.3) for a constant rate of surface deformation,  $\dot{\alpha}$ . Laplace transformation with respect to time of the problem (4.2)–(4.3) was used. The obtained equations for

the Laplace images of the concentration and the adsorption were solved and the inverse Laplace transformation of the solution was found in terms of the so-called “plasma function” [72]. Using this integral representation we obtain now the following expression for the scaled specific deformation,  $\varepsilon_D$ :

$$\varepsilon_D \equiv \frac{\varepsilon}{t_D \dot{\alpha}} = \frac{2}{\pi} \int_0^\infty [1 - \exp(-z^2 t/t_{dr})] \times [(z^2 - h_a^2/R_0^2)^2 + z^2]^{-1} dz \quad (4.7)$$

where the characteristic diffusion time,  $t_D$ , is defined as usually:  $t_D = h_a^2/D$  [7]. The solution (4.7) shows that the specific deformation,  $\varepsilon$ , in this case is function not only of the time,  $t$ , and of the rate of surface deformation,  $\dot{\alpha}$ , but depends also on the ratio between the adsorption length and the drop radius,  $h_a/R_0$ . Therefore, the geometry of the system affects  $\varepsilon$  and  $\dot{\varepsilon}$  as it can be expected. The dependence of the dimensionless specific deformation,  $\varepsilon_D$ , on the dimensionless time,  $t/t_D$ , calculated numerically for different ratios,  $h_a/R_0$ , is illustrated in Fig. 3. The dashed line corresponds to the case without diffusion, i.e. to  $\varepsilon = \alpha$ , which is equivalent to  $\varepsilon_D = t/t_D$ . One sees that the short time asymptotics,  $t \ll t_D$ , gives the solution for insoluble surfactants,  $\varepsilon = \alpha$ . The role of the drop radius on the specific deformation is pronounced—the smaller the drops are, the more intensive the bulk diffusion process is (see Fig. 3). For small drops or large adsorption lengths  $\varepsilon_D$  reaches a plateau. In this case ( $R_0 \ll h_a$ ) the steady solution of the diffusion problem holds and  $\varepsilon = t_{dr} \dot{\alpha} [1 - \exp(-t/t_{dr})]$ , which is the solution of Eq. (4.4).

We derived Eq. (4.5) by using only the definitions of the surface elastic stress,  $\tau_s$ , and the specific deformation,  $\varepsilon$ , along with the surface mass balance (4.3). Since the definitions of  $\tau_s$  and  $\varepsilon$  do not depend on the nature of the process (provided that the deformation  $\alpha$  is small) the

various surface processes involving soluble surfactants will differ only by the expressions for the bulk diffusion flux,  $J$ , which stands in the right hand side of Eq. (4.3). Since the flux is caused by the adsorption perturbation,  $\tilde{\Gamma}$ , in linear approximation  $J$  must be proportional to  $\tilde{\Gamma}$  but the factor of proportionality in the general case will be a function  $\zeta$  of time (and also of some other system parameters, such as  $D$  and possibly  $R_0$ ), i.e.  $J$  can be written as  $J = \zeta(t)\tilde{\Gamma}$ . It is not difficult to figure out, that this will lead again to Maxwell type of equation but with elasticity and apparent viscosity, which will depend on time or the frequency,  $\omega$ , for periodic oscillations. Therefore, rheological equations of the type of Eq. (4.5) will be valid for any adsorption process with small surface perturbations. No matter what the specific process is, the rheological event will always consist of bulk transport, followed by surface deformation—as already explained, this combination corresponds exactly to Maxwell model. The respective surface elasticities and characteristic times and thereby—the apparent viscosities, will depend on the nature of the specific process and will involve parameters, characteristic of it. As shown in the example with the expanding drop above, if the flux is steady, it will be equal to the product of a constant factor (specific for the process under consideration) and the perturbation  $\tilde{\Gamma}$ . Then the Maxwell elasticity and surface viscosity will be also constant. We will illustrate these considerations below by examples of barrier-controlled adsorption and oscillations of a drop and of a planar interface with diffusion controlled mass transport.

#### 4.1.2. Barrier-controlled adsorption

This case is realized when there is an adsorption barrier, slowing down the surfactant transfer onto the surface from the subsurface, where its concentration is  $c_s$ . Then the rates of adsorption,  $\tilde{r}_{ads}$ , and desorption,  $\tilde{r}_{des}$ , are different and the surfactant flux is  $J_{ads} = \tilde{r}_{ads} - \tilde{r}_{des}$ . The boundary condition (4.3) for the perturbation of the adsorption is [72]:

$$\frac{d\tilde{\Gamma}}{dt} + \Gamma_{eq} \dot{\alpha} = J_{ads} = \tilde{r}_{ads} - \tilde{r}_{des} \quad (4.8)$$

The desorption rate,  $\tilde{r}_{des}$ , is always proportional to the perturbation of the adsorption,  $\tilde{\Gamma}$ , i.e.  $\tilde{r}_{des} = k_{des} \tilde{\Gamma}$ , where the rate constant is  $k_{des}$ . The adsorption rate,  $r_{ads}$ , is proportional to the subsurface concentration,  $c_s$ , and depends on the adsorption,  $\Gamma$ , but the exact dependence on  $\Gamma$  is determined by the mechanism of adsorption. This dependence can be found from the theoretical equilibrium adsorption isotherm, which can be always written as  $K_a c_s = \Gamma/f(\Gamma)$ , where  $K_a$  is the adsorption constant and  $f(\Gamma)$  is a function, specific for every isotherm (Langmuir, Volmer, etc.). The adsorption rate is  $r_{ads} = k_{ads} c_s f(\Gamma)$ , where  $k_{ads}$  is a constant depending exponentially on the adsorption barrier. For small perturbations the adsorption rate can be linearized [72]

$$\tilde{r}_{ads} = (\partial r_{ads}/\partial c_s)_{eq} \tilde{c}_s + (\partial r_{ads}/\partial \Gamma)_{eq} \tilde{\Gamma} \quad (4.9)$$

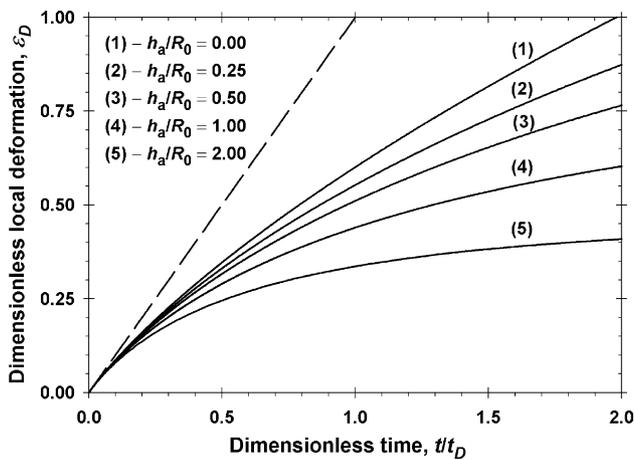


Fig. 3. Numerical solution of Eq. (4.7) for the dependence of the dimensionless specific deformation,  $\varepsilon_D$ , on the dimensionless time,  $t/t_D$  for different adsorption lengths:  $h_a/R_0 = 0.25, 0.5, 1$  and  $2$ . The dashed line (1) corresponds to  $\varepsilon = \alpha$ .

If the characteristic time of the bulk diffusion processes is much smaller than the time needed for the surfactant molecules to overcome the barrier, then the perturbation of the subsurface concentration is negligible (i.e. the subsurface concentration,  $c_s$ , is equal to the bulk surfactant concentration) and the adsorption flux is proportional to  $\tilde{\Gamma}$ . Then Eq. (4.8) is simplified to [72]:

$$\frac{d\tilde{\Gamma}}{dt} + \dot{\alpha}\Gamma_{\text{eq}} = -\frac{\tilde{\Gamma}}{t_{\text{barr}}}, \quad \frac{1}{t_{\text{barr}}} \equiv k_{\text{des}} - \left(\frac{\partial r_{\text{ads}}}{\partial \Gamma}\right)_{\text{eq}} \quad (4.10)$$

where  $t_{\text{barr}}$  is the characteristic time of the barrier-controlled adsorption process. Note, that Eq. (4.4) and (4.10) have the same form—the only difference is in the definitions of  $t_{\text{dr}}$  and  $t_{\text{barr}}$ . Therefore, in this case again the Maxwell constitutive law is valid and the apparent surface viscosity is defined with the expression,  $\eta_s^{\text{app}} = E_G t_{\text{barr}}$ .

One problem the experimentalist often faces is how to decide which model of adsorption to use: diffusion controlled or barrier controlled. The problem stems from the fact that the two fluxes are consecutive and therefore always equal. For example, for a spherical drop one has:

$$\frac{d\tilde{\Gamma}}{dt} + \Gamma_{\text{eq}}\dot{\alpha} = -\frac{\tilde{\Gamma}}{t_{\text{barr}}} = D\frac{d\tilde{c}}{dr} \quad \text{at } r = R_0 \quad (4.11)$$

The situation is similar to that of two resistors, connected in series—the current through them is the same, but if the resistances are different, the potential difference applied to each of them will be also different. The resistances can be compared if the same potential difference is applied to each resistor and the respective current is measured. In our case the role of the electric current is played by the diffusion flux, which is equal to  $J_{\text{diff}} \approx -D\tilde{\Gamma}/(h_a R_0)$ , and the adsorption flux,  $J_{\text{ads}} = -\tilde{\Gamma}/t_{\text{barr}}$ . The ratio of the fluxes,  $J_{\text{diff}}/J_{\text{ads}}$ , for the same “potential difference”,  $\tilde{\Gamma}$ , is the measure for the ratio of their “resistances”:

$$R_J = \frac{J_{\text{diff}}}{J_{\text{ads}}} \approx \frac{D/(h_a R_0)}{1/t_{\text{barr}}} = \frac{t_{\text{barr}}}{t_{\text{dr}}} \quad (4.12)$$

If  $R_J \gg 1$ , the diffusion is fast ( $t_{\text{dr}}$  is small) and the process is barrier controlled. In the opposite case it is diffusion controlled. For adsorption on a planar surface, the distance,  $r$ , must be scaled by the diffusion length,  $\delta \approx \sqrt{Dt}$ . Then  $J_{\text{diff}} \approx D\tilde{\Gamma}/(h_a \delta)$  and

$$R_J = \frac{J_{\text{diff}}}{J_{\text{ads}}} \approx \frac{Dt_{\text{barr}}}{h_a \delta} = \frac{t_{\text{barr}}}{h_a} \sqrt{\frac{D}{t}} \quad (4.13)$$

One interesting consequence from Eq. (4.13), is that at  $t \rightarrow 0$  always  $R_J \gg 1$  no matter how small  $t_{\text{barr}}$  is and the process is always barrier controlled. As time goes on,  $R_J$  becomes smaller and the process can turn into diffusion controlled. This change of adsorption mechanism was studied theoretically in more details in [72].

The fact that the mechanism of surfactant transport can change with time means that it is possible to have systems or conditions (even for the same system) when the diffusion

and the adsorption fluxes have comparable “resistances”. In such cases the mechanism of surfactant transport is mixed, with characteristic time,  $t_{\text{mix}}$ . For steady-state diffusion toward a small drop with constant  $\dot{\alpha}$  [see above (i)]  $t_{\text{mix}}$  can be obtained by eliminating  $\tilde{c}_s$  from Eq. (4.11) and replacing it in the general expression for  $\tilde{r}_{\text{ads}}$  (4.9). Thus one obtains:

$$\frac{1}{t_{\text{mix}}} = \left[ k_{\text{des}} - \left(\frac{\partial r_{\text{ads}}}{\partial \Gamma}\right)_{\text{eq}} \right] \left[ 1 + \frac{R_0}{D} \left(\frac{\partial r_{\text{ads}}}{\partial c}\right)_{\text{eq}} \right]^{-1} \quad (4.14)$$

and the apparent surface viscosity becomes  $\eta_s^{\text{app}} = E_G t_{\text{mix}}$ .

#### 4.1.3. Oscillations of a drop and a planar surface layer

For an oscillating drop  $t_{\text{def}} \approx \dot{\alpha}^{-1} \approx 1/(\omega\alpha)$  (so that the condition for steady diffusion is  $R_0^2\omega\alpha/D \ll 1$ ). Then, the steady state flux is the same as for an expanding drop, which leads again to Eqs. (4.4) and (4.5). Therefore, the apparent surface viscosity will be again  $\eta_s^{\text{app}} = E_G t_{\text{dr}}$ . It does not depend on the frequency,  $\omega$ , opposite to the case of a planar surface, considered below.

Oscillations of a planar surface can be realized either by moving quickly a barrier at the surface of a trough or more easily—by taking a large enough drop or bubble subject to oscillation with a given frequency,  $\omega$ . The amplitude and the phase shift of the surface stress are measured. For oscillations all functions are presented as their complex amplitudes multiplied by  $\exp(i\omega t)$ . The solution of the diffusion problem (4.2) for large drops (i.e. for  $R_0 \gg h_a$ ) or a flat surface can be presented, in terms of the coordinate  $x=r-R_0$ , as

$$\tilde{c} = \frac{\tilde{\Gamma}}{h_a} \exp\left[-(1+i)\sqrt{\frac{\omega}{2D}}x\right] \quad (4.15)$$

After substitution of Eq. (4.15) into the boundary condition (4.3), the following simple expression is derived:

$$\frac{d\tilde{\Gamma}}{dt} + (1+i)\frac{\tilde{\Gamma}}{2t_D}(2\omega_D)^{1/2} = -\Gamma_{\text{eq}}\dot{\alpha} \quad (4.16)$$

where the dimensionless frequency,  $\omega_D$ , is defined as  $\omega_D \equiv t_D\omega$ . Using again the definition of the specific deformation,  $\varepsilon = -\tilde{\Gamma}/\Gamma_{\text{eq}}$ , and the elastic law,  $\tau_s = E_G\varepsilon$ , Eq. (4.16) can be rewritten in the equivalent form:

$$\frac{1 + 1/(2\omega_D)^{1/2}}{E_G} \dot{\tau}_s + \frac{\omega}{E_G(2\omega_D)^{1/2}} \tau_s = \dot{\alpha} \quad (4.17)$$

This is again a Maxwell type constitutive equation as Eq. (1.5), but as anticipated above, in this case the elasticity and the apparent surface viscosity depend explicitly on time (frequency):

$$E_M = \frac{E_G(2\omega_D)^{1/2}}{(2\omega_D)^{1/2} + 1}, \quad \eta_s^{\text{app}} = \frac{E_G(2\omega_D)^{1/2}}{\omega} \quad (4.18)$$

The reason is the time dependence in (4.15) of the bulk concentration  $\tilde{c}$  and of the flux of the surfactant. For high

frequencies the apparent surface viscosity becomes negligible (because the diffusion stops) and the elasticity,  $E_M$ , is approximately equal to the Gibbs elasticity,  $E_G$ . For low frequencies one can write  $\eta_s^{\text{app}}=E_M/\omega$ . Since  $\omega$  is inverse time, this result can be also regarded as an apparent viscosity. For arbitrary frequencies  $\eta_s^{\text{app}}=E_G(2t_D/\omega)^{1/2}$  and the characteristic time is  $(2t_D/\omega)^{1/2}$ .

The first theory of oscillation of an elastic planar surface with a soluble surfactant was developed by Lucassen and van den Tempel [68,69]. They used the elastic law  $\tau_s=E_G\varepsilon$ , but since they wanted to introduce the experimental quantity surface deformation,  $\alpha$ , they wrote  $\tau_s$  also in terms of  $\alpha$ :  $\tau_s=G\alpha$ . It turned out that because of the diffusion  $G$  must be a complex quantity, which they called complex elasticity. Hence, they postulated:

$$\frac{\tau_s}{\alpha} = E_G \frac{\varepsilon}{\alpha} \equiv G = G_r + iG_i \quad (4.19)$$

The real and the imaginary parts of  $G$  ( $G_r$  and  $G_i$ , respectively) were called by these authors surface elasticity modules [68,69]. Substituting Eq. (4.19) into Eq. (4.17) expressions for  $G_r$  and  $G_i$  can be derived, if one postulates  $\alpha$  proportional to  $\exp(i\omega t)$ . The result is [68,69]:

$$G_r = E_G \frac{\omega_D + (\omega_D/2)^{1/2}}{\omega_D + (2\omega_D)^{1/2} + 1},$$

$$G_i = E_G \frac{(\omega_D/2)^{1/2}}{\omega_D + (2\omega_D)^{1/2} + 1} \quad (4.20)$$

For fast oscillations,  $\omega_D \gg 1$ , the first modulus becomes approximately equal to the Gibbs elasticity, i.e.  $G_r \approx E_G$ , and the second modulus can be used to estimate the characteristic diffusion time, because  $G_i \approx E_G/(2\omega_D)^{1/2}$ , see Eq. (4.20). In contrast, for slow oscillations,  $\omega_D \ll 1$ , both modules tend to the same value:  $G_r=G_i \approx E_G (\omega_D/2)^{1/2}$ .

Eq. (4.20) have been used by numerous researchers for interpretation of the data, obtained by the Oscillating Drop Method (ODM). Many of these researchers look at  $G_i$  as a surface viscosity and call it accordingly (in fact the quantity with dimension of surface viscosity is  $G_i/\omega$ ). So do also most of the producers of the numerous commercially available ODM apparatuses.  $G_r$  and  $G_i/\omega$  are indeed surface elasticity and surface viscosity, but for Voight model. This can be shown by comparing Eq. (4.19) with Eq. (2.26), following from Voight model for an oscillating surface. One sees immediately that these equations are identical if  $E_V=G_r$  and  $\eta_V=G_i/\omega$ . On the other hand, we showed above that for soluble non-interacting surfactants, the mechanism of the process is always consistent with Maxwell's model. The latter leads to Maxwell type rheological equations, which are the correct ones for this process. Therefore, the only correct definitions of surface elasticity and surface viscosity for an oscillating plane interface are Eq. (4.18) above. The expressions (4.20) can be used of course for data processing, but  $G_r$  and  $G_i/\omega$  do not have the correct meaning of surface elasticity and surface viscosity for the considered process.

This viewpoint is made more clear by considering the simpler case of steady-state diffusion. The respective equations for  $G_r$  and  $G_i$  are obtained from Eqs. (4.58) and (4.59) below by setting  $\eta_s=0$  and  $\eta_s^{\text{diff}}=0$ . The corresponding characteristic time is defined, as usual, as ratio of the surface viscosity and surface elasticity, i.e.  $(G_i/\omega)/G_r$ . The result is  $1/(\omega^2 t_{A,D})$ , whereas the result, following from Maxwell equation is  $t_{A,D}$ . One sees that unlike  $t_{A,D}$ , the characteristic time for the model of Lucassen and van den Tempel [68,69] depends on time (through  $\omega$ ), which should not be so for a steady-state process. Actually, Lucassen and van den Tempel never talked about “surface elasticity” and “surface viscosity” modules (which would be wrong) but only about “complex elasticity”, which is correct. Our Eq. (4.18) give the correct expressions for calculations of the rheological parameters of oscillating drops, but one must keep in mind, that these too are “apparent” quantities, similar to  $\eta_s^{\text{app}}$ , defined by Eq. (4.6).

#### 4.1.4. Apparent surface viscosity of thin liquid films

The interfacial rheology plays an important role for the drainage rate and the lifetime of thin liquid films and thereby—for the stability of foams and emulsions. The boundary condition at the film surface when solving the equation of liquid motion is  $[\tau_b]=\partial\tau_s/\partial r$  [2,15,16], where  $[\tau_b]$  is the jump of the bulk viscous stress at the film surface and  $r$  is the radial coordinate at the film surface. In the absence of surface reaction  $\tau_s=E_G\varepsilon$  and the boundary condition is:

$$[\tau_b] = E_G \frac{\partial\varepsilon}{\partial r} \quad (4.21)$$

The interfacial mass balance equation for steady state drainage of an axisymmetric thin liquid film can be presented as [2]:

$$\frac{1}{r} \frac{\partial}{\partial r} \left[ r\Gamma_{\text{eq}}u + r \left( D_s + \frac{hD}{2h_a} \right) \frac{\partial\tilde{\Gamma}}{r} \right] = 0 \quad (4.22)$$

where  $u$  is the radial component of the film surface velocity,  $h$  is the film thickness and  $D_s$  is the surface diffusion coefficient. The meaning of the terms in Eq. (4.22) is the following:  $\Gamma_{\text{eq}}u$ —is the surface convective flux;  $D_s\partial\tilde{\Gamma}/\partial r$ —is the surface diffusion flux and the last term therein appears after the solution of the bulk diffusion problem and it accounts for the bulk diffusion flux. Taking into account that the surface divergence of the surface velocity gives the rate of surface deformation,  $\dot{\alpha}$ , Eq. (4.22) is transformed into the following relationship:

$$\frac{2h_a}{2h_aD_s + hD} \dot{\alpha} - \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\varepsilon}{\partial r} \right) = 0, \quad \dot{\alpha} = \frac{1}{r} \frac{\partial}{\partial r} (ru) \quad (4.23)$$

The specific deformation,  $\varepsilon$ , can be eliminated from Eqs. (4.21) and (4.23). To avoid the integration of Eq. (4.23), which needs a boundary condition, we will apply to Eq. (4.21) the operator surface divergence and will introduce

dimensionless radial coordinate,  $\tilde{r}=r/R_f$  (scaled with the film radius,  $R_f$ ). From the result of this operation and Eq. (4.23)  $\varepsilon$  can be eliminated and one obtains:

$$\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} (\tilde{r}[\tau_b]) = \eta_f^{\text{app}} \dot{\alpha}, \quad \eta_f^{\text{app}} = \frac{2h_a E_G R_f^2}{2h_a D_s + hD} \quad (4.24)$$

The quantity  $\eta_f^{\text{app}}$  has dimension of surface viscosity and we refer to it as apparent film surface viscosity (see also [2,3], where such expressions were first derived). For real systems the film thickness,  $h$ , is of the order of 20–100 nm, the adsorption length,  $h_a$ , is of the order of microns and the bulk and the surface diffusion coefficients are of the same order of magnitude. Therefore, the expression for the apparent surface viscosity of the film can be simplified to  $\eta_f^{\text{app}} \approx E_G R_f^2 / D_s$ . Even for very small adsorptions, corresponding to  $E_G=1$  mN/m, and for typical values  $R_f=100$   $\mu\text{m}$  and  $D_s=10^{-9}$   $\text{m}^2/\text{s}$ , the apparent film surface viscosity is large:  $\eta_f^{\text{app}}=0.01$  Ns/m. For large values of  $\eta_f^{\text{app}}$  the film surfaces become tangentially immobile. The conclusion we can draw is, that it is formally possible to consider the elastic surface stress,  $E_G \varepsilon$ , as a surface viscous stress, but the results of such approach will be misleading. Some authors [73] were tempted by this possibility and replaced in the theory of film drainage the correct boundary condition (4.21) by  $[\tau_b]=\eta_f^{\text{app}} \dot{\alpha}$ . However, they disregarded the diffusion equation and considered  $\eta_f^{\text{app}}$  as true surface viscosity, which must in principle be determined by another method. That such approach is not correct is obvious from Eq. (4.24), showing that the film surface viscosity,  $\eta_f^{\text{app}}$ , is a function of the film geometry and therefore, cannot be measured by any other method. Besides,  $\eta_f^{\text{app}}$  will even change during the film drainage or expansion, due to its dependence on  $R_f$  and  $h$ . Therefore, the only way to account correctly for the film surface rheology for systems without true surface viscosity,  $\eta_s$ , is to use Eq. (4.21), along with the diffusion equation in order to calculate  $\varepsilon$ . If  $\eta_s$  is not zero, one must replace Eq. (4.21) with the appropriate expression for the surface stress,  $\tau_s$ , corresponding to the system under consideration. One possible way to find the correct expression for  $\tau_s$  is illustrated in Section 4.2.

Probably because of the apparently viscous behavior of the film surfaces, demonstrated above, there is a tendency in the literature to seek correlations between film and foam (or emulsion) stability on the one side and the imaginary part of the complex elasticity,  $G_i$ , (considered as surface viscosity) on the other, on the ground that the surface viscosity slows down the drainage, thus increasing the stability. Other people seek correlations with the damping coefficient of the surface waves, which is a similar way of thinking. In order for such correlations to be correct, the ratio of  $\eta_f^{\text{app}}$  and  $G_i/\omega$  (having dimension of surface viscosity) must be unity (or at least constant) for any values of the system parameters. This is possible only for the Expanding Drop Method, if the expansion is carried out at constant deformation rate,  $\dot{\alpha}$ . It is obvious that this is not so for any of the oscillation based

methods, since the respective elasticities and viscosities, e. g.  $G_r$  and  $G_i$ , are functions of the frequency,  $\omega$ , whereas  $\eta_f^{\text{app}}$  corresponds to zero frequency. In the limit  $\omega \rightarrow 0$ ,  $G_i$  becomes zero, while  $G_i/\omega$  is infinite-obviously neither of them can be equal in this limit to the apparent film viscosity, having finite value. On the other hand, the film surface viscosity  $\eta_f^{\text{app}}$  depends strongly on the film radius,  $R_f$ , and the surface diffusivity,  $D_s$ , (the dependence on  $h$  and  $D$  is weaker), while these quantities do not participate at all in  $G_r$  and  $G_i$ .

We will support these considerations by somewhat more quantitative analysis. From Eqs. (4.20) and (4.24) the ratio between  $G_i/\omega$ , and  $\eta_f^{\text{app}}$  is:

$$\frac{G_i/\omega}{\eta_f^{\text{app}}} = \frac{(\omega_D/2)^{1/2}}{\omega_D + (2\omega_D)^{1/2} + 1} \frac{1}{\omega_D} \frac{D_s h_a^2}{DR_f^2} \quad (4.25)$$

For fixed value of  $D_s h_a^2 / (DR_f^2)$ , the ratio  $G_i/(\eta_f^{\text{app}} \omega)$  decreases with the increase of the dimensionless frequency (see Fig. 4a). From Fig. 4a one sees that the ratio  $G_i/(\eta_f^{\text{app}} \omega)$  becomes unity at different frequencies for curves 2 and 3 and curve 1 does not reach the value 1 in the investigated

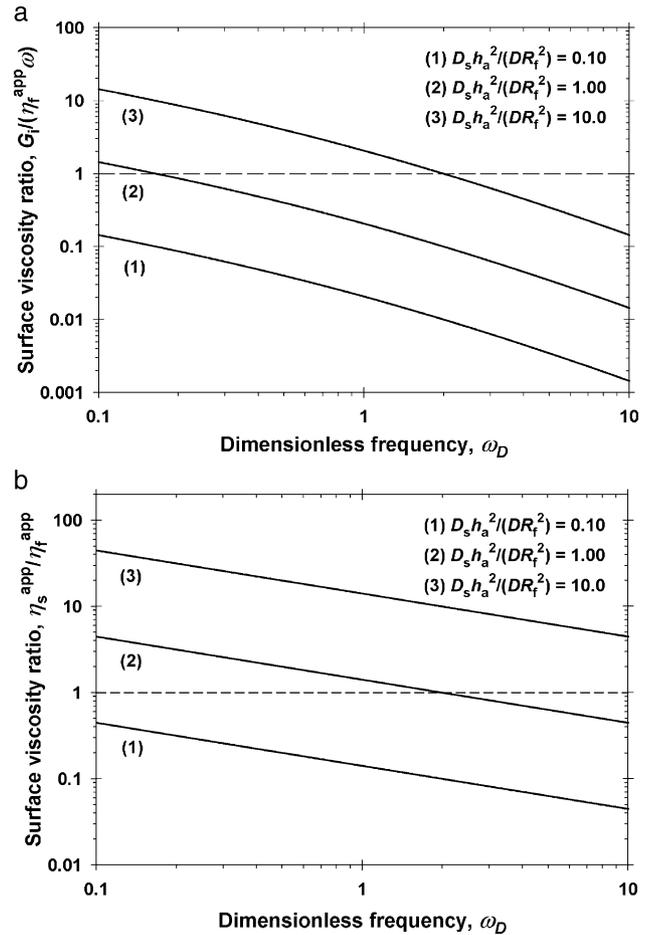


Fig. 4. Dependence of the surface viscosity ratio (a),  $G_i/(\eta_f^{\text{app}} \omega)$ , calculated from Eq. (4.25), and of the ration (b),  $\eta_s^{\text{app}}/\eta_f^{\text{app}}$ , calculated from Eq. (4.26), on the dimensionless frequency,  $\omega_D=t_D \omega$ , for three different kinds of films:  $D_s h_a^2 / (DR_f^2)=0.1, 1$  and  $10$ .

region of frequencies. Therefore, direct correlation between  $G_i$  and the film lifetime (or foam/emulsion stability) does not exist. The same conclusion is valid for the ratio of the apparent surface viscosity,  $\eta_s^{\text{app}}$  from Eq. (4.18), and the apparent surface viscosity of the film,  $\eta_f^{\text{app}}$ , from Eq. (4.24), which is:

$$\frac{\eta_s^{\text{app}}}{\eta_f^{\text{app}}} = \frac{2}{(2\omega_D)^{1/2}} \frac{D_s h_a^2}{DR_f^2} \quad (4.26)$$

Fig. 4b illustrates that the ratio  $\eta_s^{\text{app}}/\eta_f^{\text{app}}$  becomes unity at a specific frequency only for curve 2, while curves 1 and 3 do not reach the value 1 in the investigated region of frequencies.

The only connection between  $G_i$  (or  $\eta_s^{\text{app}}$ ) and  $\eta_f^{\text{app}}$  is that both are proportional to the Gibbs elasticity,  $E_G$  [compare Eqs. (4.20) and (4.24)]. It has been shown both theoretically and experimentally [2,3,74,75] that the surface tension gradient  $\partial\sigma/\partial r$ , which is proportional to the Gibbs elasticity,  $E_G$ , decreases the surface mobility and thereby—the rate of film drainage, which in turns increases the film lifetime. Since  $G_i/\omega$  and  $\eta_s^{\text{app}}$  are both proportional to  $E_G$ , it should not be surprising that correlation between them and the film lifetime could exist. Similar correlation could exist however only for the drainage of unstable films or the lifetime of unstable foams and emulsions, where coalescence between bubbles or drop occurs.

The situation is even more confusing if the comparison between surfactants is done as a function of their bulk concentration,  $c$ . The surfactant is characterized not only by its Gibbs elasticity  $E_G$ , but also by its adsorption thickness,  $h_a = (\partial\Gamma/\partial c)_{\text{eq}}$ , which enters into the dimensionless frequency,  $\omega_D = t_D\omega$ . The quantities  $E_G$  and  $h_a$  have opposite dependence on  $c$ , as illustrated for Langmuirian adsorption in Fig. 5a. Besides, because of the complicated dependence of  $G_i$  on  $\omega_D$ , the relative contribution of  $E_G$  and  $h_a$  to  $G_i$  will depend on the frequency,  $\omega$ . Hence, it may turn out that at one frequency given surfactant seems more efficient stabilizer than another one, while at another frequency the opposite may seem true—such behavior is illustrated in Fig. 5b. Therefore, if the experimentalist has no information on  $E_G$  and  $h_a$ , the comparison of surfactants, based on  $G_i$ , may lead to erroneous conclusion. Briefly, similar correlations, based on  $G_i$  or  $G_i/\omega_i$ , are misleading not only insofar as the mechanism of the process is concerned, but can lead even to erroneous qualitative conclusions.

The apparent surface viscosity,  $\eta_s^{\text{app}}$ , defined by Eq. (4.18), which follows from Maxwell equation (4.17), also depends on the frequency, but in a very simple way:  $\eta_s^{\text{app}}$  is proportional to  $\omega^{-1/2}$ , i.e. the frequency serves only as a scaling factor. This is illustrated in Fig. 5c, which is calculated with the same parameters values as Fig. 5b. One sees that if one compares two surfactants, their relative efficiency will not depend on frequency. In fact, if one plots  $\eta_s^{\text{app}}\omega^{1/2}$  vs. surfactant concentration  $c$ , there will be no frequency dependence and the resulting curve

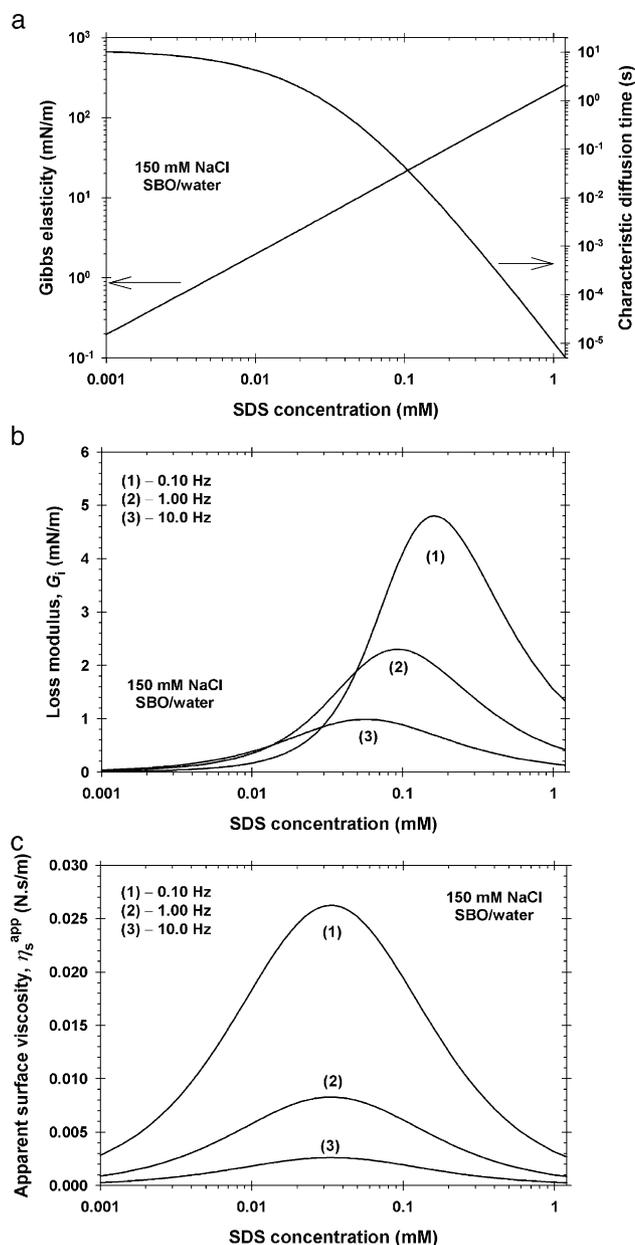


Fig. 5. Dependence of the Gibbs elasticity,  $E_G$ , and the diffusion relaxation time,  $t_D$ , (a) and the loss modulus,  $G_i$ , (b), on the surfactant concentration. The parameters of the Langmuir adsorption isotherm for sodium dodecyl sulfate (SDS) at the soybean oil/water interface in the presence of 150 mM NaCl are adsorption constant, 29.9 1/mM;  $\Gamma_\infty = 2.66 \mu\text{mol}/\text{m}^2$ ;  $D = 5.5 \times 10^{-10} \text{ m}^2/\text{s}$ .

(which will have the same shape as those in Fig. 5c) will depend only on the surfactant properties and concentration. Therefore, at least qualitatively, correlations of the lifetimes of unstable films, foams and emulsions with  $\eta_s^{\text{app}}$  will be more reliable, that those with  $G_i$  or  $G_i/\omega$ . Measurements of the apparent surface viscosity,  $\eta_s^{\text{app}}$ , can be used also for determining directly (provided that the diffusivity  $D$  is known) the equilibrium adsorption isotherm  $\Gamma_{\text{eq}} = \Gamma_{\text{eq}}(c)$  (and possibly—the kinetics of adsorption) without resorting to differentiation of the

dependence  $\sigma_{\text{eq}} = \sigma_{\text{eq}}(c)$ . Indeed, it is difficult to show from Eq. (4.18) along with the definitions of the Gibbs elasticity,  $E_G$ , and the absorption length,  $h_a$ , that  $c\eta_s^{\text{app}}(\omega D/2)^{1/2} = E_G(\partial\Gamma/\partial\ln c)_{\text{eq}} = k_B T \Gamma^2$ . If the surfactant obeys the Langmuir adsorption isotherm the position of the maximum of  $\eta_s^{\text{app}}(c)$  (see Fig. 5c) will be located at  $c_{\text{max}} = 1/K$ , where  $K$  is the adsorption constant. Similar results can be obtained for other adsorption isotherms as well (Volmer, Frumkin, etc.).

Such correlations between film (or foam and emulsion) lifetime and  $G_i$  have even less foundations in cases when the films eventually become stable, i.e. when they reach equilibrium at a certain thickness. The equilibrium state has no relation to the surface mobility. Indeed, the Gibbs elasticity can only slow down the film drainage but cannot arrest it and make the film stable—only the disjoining pressure,  $\Pi$ , can do it. Besides, our results [2–5] show that even minor surfactant concentration (corresponding to  $E_G \approx 1$  mN/m) is sufficient to suppress almost entirely the surface mobility. Above this concentration the effect of the surfactant on the film lifetime and on the foam or emulsion stability is entirely controlled by the disjoining pressure,  $\Pi$ . The main stabilizing components of  $\Pi$  (the electrostatic and the steric ones) are related to and increase with the adsorption  $\Gamma$ . The increased adsorption,  $\Gamma$ , which leads to increased  $\Pi$  and thereby—to larger film lifetime, is paralleled by increased Gibbs elasticity and according to Eq. (4.20)—by increased  $G_i/\omega$ . However, this parallelism does not mean that the film stability is due to the increased Gibbs elasticity and for that matter—to the “pseudo-viscosity”. These are completely different effects, having only the same origin (the surfactant adsorption) but independent of each other. Since the effect of  $\Pi$  has thermodynamic nature and that of  $E_G$  is kinetic, it seems needless to stress that this kind of correlation between film, foam and emulsion stability on the one side and the “pseudo-viscosity” on the other, lacks scientific background.

#### 4.2. Coupling of diffusion and surface reaction

The rheological equations in Sections 2 and 3 were written only in terms of surface variables:  $\varepsilon_k^s$ ,  $\dot{\varepsilon}_k^s$ ,  $\alpha$ ,  $\dot{\alpha}$ , etc. However, in the case of soluble surfactants the surface is no longer autonomous, since the diffusion fluxes affect the surface variables—implicitly, by changing  $\varepsilon_k^s$  and  $\dot{\varepsilon}_k^s$  and explicitly, through the difference  $\dot{\varepsilon}_k^s - \dot{\alpha}$ , which is proportional to the bulk diffusion flux  $J_k$  [see Eq. (3.38)]. On the other hand, the experimentalist can control the bulk concentrations,  $c_k$ , the deformation,  $\alpha$ , and its rate,  $\dot{\alpha}$ , but not the specific variables  $\varepsilon_k^s$  and  $\dot{\varepsilon}_k^s$ . For this reason in this subsection we will proceed by expressing  $\varepsilon_k^s$  and  $\dot{\varepsilon}_k^s$  through the experimental variables in order to find a complete surface rheological equation suitable for interpretation of experimental data. Because of the complexity of the problem, we will only sketch a general method for obtaining solution, but will illustrate in more details the

approach to be followed on the relatively simple example of dimerization.

In many cases one or more small parameters can be formulated, which allows asymptotic solution and sometimes complete decoupling of the surface reaction from the mass transport problem. We will formulate below the general principles of one possible approach leading to Voigt type rheological equations. The procedure to be followed is best illustrated by the general Eq. (3.21) of the relaxation process. It involves two characteristic times: of the reaction,  $t_r$  (through  $\zeta_r$ ) and of the deformation  $t_{\text{def}} = 1/\dot{\alpha}$  (through  $\zeta_{\text{eq}}$ ). Introducing dimensionless times for the reaction,  $t'_r = t/t_r$  for the derivative  $\partial\zeta_r/\partial t$  and  $t' = t/t_{\text{def}}$  for  $d\zeta_{\text{eq}}/dt$ , one can rewrite (3.21) as:

$$\frac{d\zeta_r}{dt'_r} + \zeta_r = -\beta \frac{d\zeta_{\text{eq}}}{dt'} \quad (4.27)$$

where  $\beta = t_r/t_{\text{def}}$ . The limit  $\beta = 0$  corresponds to infinitely slow deformation. The function  $\zeta_{\text{eq}}$ , given by Eq. (3.20), corresponds to the quasi-equilibrium state, which was defined in Section 2 by the condition  $t_r/t_{\text{def}} = 0$ . Therefore, it cannot depend on  $t_r$ , so that the product  $v_{\text{eq}}t_r$ , according to Eq. (2.11) does not depend on  $t_r$  either. Setting in (4.27)  $\beta = 0$  one obtains for the zeroth approximation of  $\zeta_r$ :

$$\frac{d\zeta_r^0}{dt'_r} + \zeta_r^0 = 0, \quad \zeta_r^0 = \zeta(0)\exp(-t/t_r) \quad (4.28)$$

For a perturbation starting from equilibrium (which has been assumed throughout the present article)  $\zeta(0) = 0$ ,  $\zeta_r^0 = 0$  and  $\zeta^0 = \zeta_{\text{eq}} + \beta\zeta_r^0 = \zeta_{\text{eq}}$ , i.e. this case corresponds to quasi-equilibrium. Indeed, since the expansion is very slow when  $\beta = 0$ , the reaction is capable of maintaining the equilibrium in any moment. The function  $\zeta_r^0$  may not be zero, if the relaxation starts from some initial perturbation  $\zeta_r(0) \neq 0$ , which is (approximately) realized in the relaxational rheological methods (see the Introduction)—we will not consider this case in the present article. If one wants to determine the next approximations, one must represent  $\zeta_r$  as a series of  $\beta$ :  $\zeta_r = \zeta_r^0 + \beta\zeta_r^1$ , determine the functions,  $\zeta_r^0$ ,  $\zeta_r^1$ , etc., by substituting the series in Eq. (4.27) and the initial condition  $\zeta_r(0) = 0$  and solving the ensuing equations for different powers of  $\beta$  (for details see [76]). Then the first approximation  $\zeta_r^1$  will satisfy the equation:

$$\frac{d\zeta_r^1}{dt'_r} + \zeta_r^1 = -\frac{d\zeta_{\text{eq}}}{dt'} \quad (4.29)$$

All higher order approximations satisfy equations of the type of Eq. (4.28), which means that they are identically zero. Thus we reach the conclusion that for  $\beta \ll 1$ ,  $\zeta_r$  is represented only by the term, proportional to  $\beta$ .

The reasons for this result can be understood by the behavior of  $\zeta_r$  for insoluble surfactants, corresponding only to the first term in the right hand side of (3.30). The exact solution for constant  $\dot{\alpha}$  is [cf. (2.14) and (2.33)]

$$\zeta_r = - (v_{\text{eq}}t_r v) \beta [1 - \exp(-t'/\beta)] \quad (4.30)$$

Since all derivatives of  $\exp(-t'/\beta)$  with respect to  $\beta$  are zero at  $\beta=0$ , its expansion in powers of  $\beta$  is identically zero and the asymptote of  $\tilde{\xi}_r$  at  $\beta \ll 1$  is proportional only to  $\beta$  (recall that according to Eq. (2.11)  $v_{\text{eq}}t_r$  does not depend on  $t_r$ ). This corresponds to the result we obtained above for the more general case of soluble surfactants.

The same procedure will be applied below to all other equations describing the process. They contain however time derivatives, which may have different characteristic times. For convenience we will choose  $t_{\text{def}}$  to characterize all processes (besides the surface reaction) since this time is the only variable, directly in control of the experimentalist. Such an approach is legitimate if all other characteristic times are larger than  $t_r$ . After writing the equations, corresponding to different powers of  $\beta$ , additional simplifications are possible, depending on the ratio of the relaxation times. The realization of the above general procedure is illustrated below for the reaction of surface dimerization.

#### 4.2.1. Decoupling of the diffusion problem and the rheological equation

The mass balance boundary conditions for the perturbations of the adsorptions of the monomers,  $\tilde{\Gamma}_1$ , and the dimmers,  $\tilde{\Gamma}_2$ , are [see Eqs. (2.47–2.50), (3.14) and (4.3)]:

$$\frac{d\tilde{\Gamma}_1}{dt} + \Gamma_{1,\text{eq}}\dot{\alpha} = -\frac{D\tilde{c}_s}{R_0} - 2k^- \Gamma_{2,\text{eq}}(2a_1\tilde{\Gamma}_1 - a_2\tilde{\Gamma}_2) \quad (4.31)$$

$$\frac{d\tilde{\Gamma}_2}{dt} + \Gamma_{2,\text{eq}}\dot{\alpha} = k^- \Gamma_{2,\text{eq}}(2a_1\tilde{\Gamma}_1 - a_2\tilde{\Gamma}_2) \quad (4.32)$$

Throughout this paper we have been using the assumption for local equilibrium, implying that the instantaneous values of the adsorption,  $\Gamma_k(t)$ , be connected with the instantaneous values of the surface pressure,  $\pi(t)$ , and the subsurface concentration,  $c_{k,s}(t)$ , through the equilibrium isotherms,  $\pi=\pi(\Gamma_1, \dots, \Gamma_n)$  and  $c_{k,s}=c_{k,s}(\Gamma_1, \dots, \Gamma_n)$  [see assumption (iii) in Section 2]. Therefore, the subsurface concentration is determined by the adsorptions. The latter however depends on the surface mass balance, involving also the chemical reaction. Because of this coupling between mass transport and reaction, the subsurface concentration of component 1 in the reaction of dimerization depends not only on  $\Gamma_1$ , but also on  $\Gamma_2$ , since the dimmers can release monomers during the reaction. Besides, in the mixed adsorbed layer of monomers and dimmers  $\Gamma_1$ ,  $\Gamma_2$  and  $c_{1,s}$  are connected also through the adsorption isotherm,  $c_{1,s}=c_{1,s}(\Gamma_1, \Gamma_2)$ . This means that in spite of the fact that only the monomers are in direct equilibrium with the subsurface,  $c_{1,s}$  will depend on  $\Gamma_2$  through the adsorption isotherm.

Therefore, for diffusion-controlled adsorption the perturbation  $\tilde{c}_s$  of the subsurface concentration,  $c_s$ , will be:

$$\tilde{c}_s = \left( \frac{\partial c}{\partial \Gamma_1} \right)_{\text{eq}} \tilde{\Gamma}_1 + \left( \frac{\partial c}{\partial \Gamma_2} \right)_{\text{eq}} \tilde{\Gamma}_2 \quad (4.33)$$

If Eq. (4.33) is substituted into the first term in the right hand side of Eq. (4.31), this term becomes  $-(\tilde{\Gamma}_1/t_{D,1} + \Gamma_2/t_{D,2})$ , where

$$\begin{aligned} \frac{1}{t_{D,1}} &\equiv \frac{D}{R_0} \left( \frac{\partial c}{\partial \Gamma_1} \right)_{\text{eq}} = \frac{D}{R_0 h_{1,a}}, \\ \frac{1}{t_{D,2}} &\equiv \frac{D}{R_0} \left( \frac{\partial c}{\partial \Gamma_2} \right)_{\text{eq}} = \frac{D}{R_0 h_{2,a}} \end{aligned} \quad (4.34)$$

are diffusion times for the component 1 and 2, respectively. While  $t_{D,1}$  is direct analog of  $t_D$  for diffusion of a single component, the meaning of  $t_{D,2}$  calls for some explanation because it is apparently diffusion time for the non-soluble and the non-diffusing component 2. In fact, the true diffusion time accounting for the connection between the adsorption  $\Gamma_2$  and the bulk concentration  $c_2$  of the component 2 (if it were soluble) would have been proportional to  $(\partial \Gamma_2 / \partial c_2)_{\text{eq}}$ , which is of course infinity for insoluble surfactants. In reality,  $t_{D,2}$  in Eq. (4.34), connecting the adsorption of component 2 with the subsurface concentration of component 1 reflects the influence of the perturbation of  $\Gamma_2$  (due to the surface deformation and the chemical reaction) on the adsorption  $\Gamma_1$ , which translates into a change of the subsurface concentration  $c_s$  of component 1.

Using Eqs. (4.33) and (4.34) and introducing the dimensionless time,  $t'=t/t_{\text{def}}$ , and replacing the rate constant  $k^-$  with the expression (2.49) for the relaxation time,  $t_r$ , the mass balance boundary conditions (4.31) and (4.32) are transformed into the following asymptotic problem:

$$\begin{aligned} \beta \left( \frac{d\tilde{\Gamma}_1}{dt'} + \Gamma_{1,\text{eq}} + \frac{t_{\text{def}}}{t_{D,1}} \tilde{\Gamma}_1 + \frac{t_{\text{def}}}{t_{D,2}} \tilde{\Gamma}_2 \right) \\ = -\frac{2}{4a_1 + a_2} (2a_1\tilde{\Gamma}_1 - a_2\tilde{\Gamma}_2) \end{aligned} \quad (4.35)$$

$$\beta \left( \frac{d\tilde{\Gamma}_2}{dt'} + \Gamma_{2,\text{eq}} \right) = \frac{1}{4a_1 + a_2} (2a_1\tilde{\Gamma}_1 - a_2\tilde{\Gamma}_2) \quad (4.36)$$

where the small parameter  $\beta$  appears only in the left hand sides of Eqs. (4.35) and (4.36). Following the usual asymptotic procedure [76] the perturbations in the adsorptions can be presented as asymptotic series of the zeroth, first, second, etc. approximations:  $\tilde{\Gamma}_1 = \tilde{\Gamma}_1^0 + \beta \tilde{\Gamma}_1^1 + \beta^2 \tilde{\Gamma}_1^2 + \dots$  and  $\tilde{\Gamma}_2 = \tilde{\Gamma}_2^0 + \beta \tilde{\Gamma}_2^1 + \beta^2 \tilde{\Gamma}_2^2 + \dots$ . These series are replaced in Eqs. (4.35) and (4.36) and the terms proportional to given power of  $\beta$  are set equal. Setting  $\beta$  equal to zero, we obtain for the zeroth order approximation, the relation

$$2a_1 \tilde{\Gamma}_1^0 = a_2 \tilde{\Gamma}_2^0 \quad (4.37)$$

The perturbations  $\tilde{\Gamma}_1^0$  and  $\tilde{\Gamma}_2^0$  above pertain to the quasi-equilibrium state and are therefore, functions of the time  $t$ . These functions are determined from the first order approximation.

From the terms proportional to the first power of  $\beta$ , the following first order approximation problem is obtained:

$$\begin{aligned} \frac{d\tilde{\Gamma}_1^0}{dt'} + \Gamma_{1,\text{eq}} + \frac{t_{\text{def}}}{t_{D,1}} \tilde{\Gamma}_1^0 + \frac{t_{\text{def}}}{t_{D,2}} \tilde{\Gamma}_2^0 \\ = -\frac{2}{4a_1 + a_2} (2a_1 \tilde{\Gamma}_1' - a_2 \tilde{\Gamma}_2') \end{aligned} \quad (4.38)$$

$$\frac{d\tilde{\Gamma}_2^0}{dt'} + \Gamma_{2,\text{eq}} = \frac{1}{4a_1 + a_2} (2a_1 \tilde{\Gamma}_1' - a_2 \tilde{\Gamma}_2') \quad (4.39)$$

We multiply Eq. (4.39) by 2 and the result is added to Eq. (4.38) in order to eliminate the reaction term [the right hand side of Eqs. (4.38) and (4.39)] from the problem. In this way we represent the adsorptions as functions of the mass adsorption  $\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0$ , i.e.  $\tilde{\Gamma}_1^0 = a_2(\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0)/(4a_1 + a_2)$  and  $\tilde{\Gamma}_2^0 = 2a_1(\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0)/(4a_1 + a_2)$ . As a result of these transformations we obtain the following equation for  $\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0$ :

$$\frac{d}{dt'} (\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0) + (\Gamma_{1,\text{eq}} + 2\Gamma_{2,\text{eq}}) + \frac{t_{\text{def}}}{t_{A,\text{dr}}} (\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0) = 0 \quad (4.40)$$

where the characteristic diffusion time,  $t_{A,\text{dr}}$ , is defined as

$$\frac{1}{t_{A,\text{dr}}} \equiv \frac{1}{4a_1 + a_2} \left( \frac{a_2}{t_{D,1}} + \frac{2a_1}{t_{D,2}} \right) \quad (4.41)$$

If the definition of the specific deformation (3.13) is used, one has  $\varepsilon_s \equiv -(\tilde{\Gamma}_1^0 + 2\tilde{\Gamma}_2^0)/(\Gamma_{1,\text{eq}} + 2\Gamma_{2,\text{eq}})$  and Eq. (4.40) transforms into the mass balance boundary condition for the zeroth order specific deformation,  $\varepsilon_s^0$ , written as:

$$\frac{d\varepsilon_s^0}{dt} + \frac{\varepsilon_s^0}{t_{A,\text{dr}}} = \dot{\alpha} \quad (4.42)$$

Eq. (4.42) is similar in form to Maxwell Eq. (4.5) but have different physical meaning: while Maxwell equation refers to a single component,  $\varepsilon_s$  in Eq. (4.42) refers to a mixture of the components in the quasi-equilibrium state, which in turns is a function of time.

There are two main advantages in using Eq. (4.42):

- (i) Its solution does not depend on the rheological Eq. (4.1), i.e. the diffusion problem is decoupled from the rheological equation;
- (ii) The characteristic diffusion time,  $t_{A,\text{dr}}$ , can be determined from static experiments. To show that, let us simplify the definition (4.41) by using the equilibrium adsorption isotherm. In terms of the individual adsorptions,  $\Gamma_{1,\text{eq}}$  and  $\Gamma_{2,\text{eq}}$ , we can write:

$$\begin{aligned} dc_s &= \left( \frac{\partial c}{\partial \Gamma_1} \right)_{\text{eq}} d\Gamma_{1,\text{eq}} + \left( \frac{\partial c}{\partial \Gamma_2} \right)_{\text{eq}} d\Gamma_{2,\text{eq}} \\ &= \left( \frac{1}{h_{1,a}} + \frac{2a_1}{a_2} \frac{1}{h_{2,a}} \right) d\Gamma_{1,\text{eq}} \end{aligned} \quad (4.43)$$

where we have used the fact that according to the equilibrium constant of the reaction the adsorption  $\Gamma_{2,\text{eq}}$  is a function of  $\Gamma_{1,\text{eq}}$ , so that  $(\partial \Gamma_2 / \partial \Gamma_1)_{\text{eq}} = 2\Gamma_{2,\text{eq}} / \Gamma_{1,\text{eq}} = 2a_1 / a_2$ . On the other hand, from the experimental adsorption isotherm,  $A = A(c_s)$ , one can write in a similar way:

$$\begin{aligned} dc_s &= \left( \frac{\partial c}{\partial A} \right)_{\text{eq}} dA_{\text{eq}} = \frac{a_2 + 4a_1}{h_{A,a} a_2} d\Gamma_{1,\text{eq}}, \\ h_{A,a} &\equiv \frac{1}{M_1} \left( \frac{\partial A}{\partial c} \right)_{\text{eq}} \end{aligned} \quad (4.44)$$

where  $h_{A,a}$  is the experimental adsorption thickness, which can be determined from static experiments. By eliminating  $dc_s$  from Eqs. (4.43) and (4.44) and comparing the result with the definition (4.41) we finally find:

$$t_{A,\text{dr}} = \frac{R_0 h_{A,a}}{D} \quad (4.45)$$

In this way we succeeded to replace the two times,  $t_{D,1}$  and  $t_{D,2}$ , by a single experimentally accessible time,  $t_{A,\text{dr}}$ , which is the counterpart of  $t_{\text{dr}}$  for the case of adsorption with surface reaction.

Although we know already  $\tilde{\Gamma}_2^0(t)$  from the solution of Eqs. (4.37) and (4.40)] we cannot use the first order Eq. (4.39) to determine  $\tilde{\Gamma}_2'$ , since it contains also  $\tilde{\Gamma}_1'$ . The solution for the first order approximation can be determined by means of the second order approximation. Using the same algorithm as above we write the equations for the second order approximation, multiply the second equation by 2 and add the result to the respective first equation. The final result reads:

$$\frac{d}{dt'} (\tilde{\Gamma}_1' + 2\tilde{\Gamma}_2') + \frac{t_{\text{def}}}{t_{D,1}} \Gamma_1' + \frac{t_{\text{def}}}{t_{D,2}} \tilde{\Gamma}_2' = 0 \quad (4.46)$$

The solution of the system (4.39) and (4.46) determines  $\Gamma_1'$  and  $\Gamma_2'$  and the first order approximation of the specific deformation,  $\varepsilon_s' \equiv -(\tilde{\Gamma}_1' + 2\tilde{\Gamma}_2')/(\Gamma_{1,\text{eq}} + 2\Gamma_{2,\text{eq}})$ . The system (4.39) and (4.46) is linear and its solution is easy, but bulky. Since it refers only to the specific reaction of dimerization and has little importance for the discussion below, we will omit it.

After having found the expressions for the approximations of  $\varepsilon_s$ , we can turn to deriving the asymptotic expression of the general rheological Eq. (4.1). The surface viscosities  $\eta_s$  and  $\eta_s^{\text{diff}}$  are proportional to the relaxation time,  $t_r$ , according Eqs. (2.24) and (3.37). In all derivatives in (4.1) we will introduce now the dimensionless time  $t' = t/t_{\text{def}}$ . Having in mind that according to Eq. (2.24)  $\eta_s = E_s t_r$  and introducing the small parameter  $\beta = t_r/t_{\text{def}}$  from Eq. (4.1) we obtain for  $\tau_s$ :

$$\tau_s = E_s \varepsilon_s - \beta \frac{d}{dt'} (\tau_s - E_s \varepsilon_s) + \beta \frac{d}{dt'} \left[ \frac{\eta_s}{t_r} \varepsilon_s + \frac{\eta_s^{\text{diff}}}{t_r} (\varepsilon_s - \alpha) \right] \quad (4.47)$$

The asymptotic series for  $\tau_s$  is  $\tau_s = \tau_s^0 + \beta\tau_s^1 + \dots$  and therefore, the zeroth order approximation of Eq. (4.47) gives the elastic law:

$$\tau_s^0 = E_s \varepsilon_s^0 \quad (4.48)$$

The respective first order approximation, along with Eq. (4.48), yields:

$$\tau_s^1 = E_s \varepsilon_s^1 + \frac{d}{dt} \left[ \frac{\eta_s}{t_r} \varepsilon_s^0 + \frac{\eta_s^{\text{diff}}}{t_r} (\varepsilon_s^0 - \alpha) \right] \quad (4.49)$$

Writing down the remaining terms in dimensional form up to the linear term with respect to  $\beta$ , from Eqs. (4.48) and (4.49) we obtain the final result:

$$\tau_s = E_s \varepsilon_s^0 + \beta E_s \varepsilon_s^1 + \eta_s \dot{\varepsilon}_s^0 + \eta_s^{\text{diff}} (\dot{\varepsilon}_s^0 - \dot{\alpha}) \quad (4.50)$$

The analysis of the system (4.39) and (4.46) shows, that the resulting solution for  $\varepsilon_s^1$  is proportional to  $\Gamma_{2,\text{eq}}/\Gamma_{1,\text{eq}}$ , which is presumably small, because the van der Waals interactions between the monomers are weak (see Section 2.3). If the term with  $\varepsilon_s^1$  in Eq. (4.50) is neglected, the rheological Eq. (4.1) is finally simplified to

$$\tau_s = E_s \varepsilon_s + \eta_s \dot{\varepsilon}_s + \eta_s^{\text{diff}} (\dot{\varepsilon}_s - \dot{\alpha}) \quad (4.51)$$

where the specific deformation,  $\varepsilon_s$ , is a solution of the decoupled mass balance boundary condition (4.42). The asymptotic form (4.51) differs from the original Eq. (4.1) in two respects: first, by the neglect in the latter of the first two terms, proportional to  $t_r$  and second, by the fact that all  $\varepsilon_s$  are replaced by their zeroth approximations. If the term  $\dot{\varepsilon}_s - \dot{\alpha}$  is expressed from Eq. (4.42) and the result is substituted into Eq. (4.52) one obtains:

$$\tau_s = \left( E_s - \frac{\eta_s^{\text{diff}}}{t_{A,\text{dr}}} \right) \varepsilon_s + \eta_s \dot{\varepsilon}_s \quad (4.52)$$

Although with more complicated expression for the elasticity (due to the diffusion and the reaction), Eq. (4.52) has the same form as the rheological equation, suggested by us in [17,18,27] [see Eq. (3.2) in [17] or Eq. (1.13) in the Introduction]. This confirms our main idea, that the surface stress for soluble surfactants must depend on the specific variables (in this case,  $\varepsilon_s$  and  $\dot{\varepsilon}_s$ ) rather than on the total deformation  $\alpha$  and its rate,  $\dot{\alpha}$ .

The same procedure could be of course applied to the general Eq. (3.30) for a multicomponent system and we would obtain then (3.32). The important new finding is that the variables  $\varepsilon_k^s$  are zeroth order quantities, which correspond to the quasi-equilibrium state and can be found by separate solution of the respective diffusion problem.

Since Eq. (4.42) is analogous to the Maxwell Eqs. (4.5) whereas (4.51) corresponds to Voight model, the combination of the two models may lead to a reach variety of rheological equations, especially for multicomponent sys-

tems. The situation is additionally complicated by the fact, that  $\varepsilon_s$  and  $\dot{\varepsilon}_s$  may have themselves elastic or viscous contributions, depending on the value of  $t/t_{A,\text{dr}} = (t_{\text{def}}/t_{A,\text{dr}})t'$ . Hence, we believe that the complete rheological analysis must be made for every experimental system for given experimental conditions. Two particular cases are discussed below.

#### 4.2.2. Surfactant transport toward small spherical drops with diffusion or barrier-controlled adsorption

In the general case of diffusion toward spherical drops the solution of the decoupled diffusion problem (4.7) is a complex function of time. The situation is much simpler if the drop is small. Then the diffusion equation is reduced to Eq. (4.42), which has the same form as the transport equation in the case of barrier-controlled adsorption (4.10). Therefore, we can describe both problems with one equation using for small drops,  $t_{A,D} = t_{A,\text{dr}}$ , and for barrier-controlled adsorption,  $t_{A,D} = t_{A,\text{barr}}$ . In the case of constant total rate of deformation,  $\dot{\alpha}$ , the solution of the respective problems is obtained from Eq. (4.42):

$$\varepsilon_s^0 = \dot{\alpha} t_{A,D} [1 - \exp(-t/t_{A,D})] \quad (4.53)$$

The specific deformation,  $\varepsilon_s^0$ , from Eq. (4.53) is substituted into the rheological Eq. (4.51) to obtain:

$$\begin{aligned} \tau_s = & (E_s t_{A,D} - \eta_s^{\text{diff}}) \dot{\alpha} [1 - \exp(-t/t_{A,D})] \\ & + \eta_s \dot{\alpha} \exp(-t/t_{A,D}) \end{aligned} \quad (4.54)$$

Note that from experimental viewpoint Eq. (4.54) has only one adjustable parameter—the surface viscosities,  $\eta_s$ , since  $\eta_s^{\text{diff}}$  is simply related to  $\eta_s$  through Eq. (3.37). Besides, since  $\eta_s \alpha t_r$ , the general assumption for decoupling,  $t_r \ll t_{A,D}$ , for most real systems will lead to  $E_s t_{A,D} \gg \eta_s^{\text{diff}}$  so that  $\eta_s^{\text{diff}}$  can be neglected. All other parameters can be calculated from static equilibrium experiments. Eq. (4.54) shows that for slow deformations ( $t_{\text{def}}/t_{A,D} \gg 1$ ) the stress becomes purely viscous:

$$\tau_s = E_s t_{A,D} \dot{\alpha} \quad (4.55)$$

In contrast, for fast deformations ( $t_{\text{def}}/t_{A,\text{dr}} \ll 1$ ) it acquires the Voight form for insoluble surfactants:

$$\tau_s = E_s \alpha + \eta_s \dot{\alpha} \quad (4.56)$$

In the case of oscillations of the surface with a frequency,  $\omega$ , all functions are proportional to  $\exp(i\omega t)$ . Therefore, the rheological Eq. (4.51) can be written as:

$$\frac{\tau_s}{\alpha} = E_s \frac{\varepsilon_s^0}{\alpha} + i\omega (\eta_s + \eta_s^{\text{diff}}) \frac{\varepsilon_s^0}{\alpha} - i\omega \eta_s^{\text{diff}} \quad (4.57)$$

Eq. (4.42) relates the specific deformation,  $\varepsilon_s^0$ , and the surface deformation:  $\varepsilon_s^0/\alpha = it_{A,D}\omega/(1+it_{A,D}\omega)$ . After substituting this expression into the rheological Eq. (4.57) and presenting the result in the Lucassen and van den Tempel form (4.19), the following expressions for the real,  $G_r$ , and

imaginary,  $G_i$ , parts are obtained (note that they account also for the true surface viscosity):

$$G_r = \frac{\omega^2 t_{A,D}^2}{1 + \omega^2 t_{A,D}^2} \left( E_s - \frac{\eta_s}{t_{A,D}} - \frac{\eta_s^{\text{diff}}}{t_{A,D}} \right) \quad (4.58)$$

$$G_i = \frac{\omega t_{A,D}}{1 + \omega^2 t_{A,D}^2} \left( E_s + \omega^2 t_{A,D} \eta_s - \frac{\eta_s^{\text{diff}}}{t_{A,D}} \right) \quad (4.59)$$

In the particular case of slow deformations ( $t_{A,D} \omega \ll 1$ ) the real part,  $G_r$ , becomes very small,  $G_r \approx 0$ , and only the imaginary part,  $G_i$ , remains:  $G_i \approx \omega t_{A,D} E_s$  [see also Eq. (4.55), derived for constant rate of total deformation, which has also only viscous term]. In the opposite case of fast deformations ( $t_{A,D} \omega \gg 1$ ) Eqs. (4.58) and (4.59) are simplified to:

$$G_r \approx E_s, \quad G_i \approx \omega \eta_s \quad (4.60)$$

Note, that the same results for  $G_r$  and  $G_i$  as in Eq. (4.60) follow from Eq. (4.56) if it is written for periodic oscillations.

#### 4.2.3. Rheological model for small oscillations of a planar surface layer

When the characteristic time of the diffusion process is larger than the relaxation time,  $t_r$ , the solution of the diffusion problem is decoupled from the rheological equation. For that reason we can use the Lucassen and van den Tempel expression:

$$\frac{\varepsilon_s^0}{\alpha} = \frac{\omega_{A,D} + (\omega_{A,D}/2)^{1/2} + i(\omega_{A,D}/2)^{1/2}}{\omega_{A,D} + (2\omega_{A,D})^{1/2} + 1} \quad (4.61)$$

modified by using the characteristic diffusion time,  $t_{A,D}$  (instead of  $t_D$ ), calculated with the experimental value of the adsorption length,  $h_{A,a}$  (instead of  $h_a$ ), i.e.  $t_{A,D} = h_{A,a}^2/D$ . The dimensionless frequency is  $\omega_{A,D} = t_{A,D} \omega$ . If the solution (4.61) is substituted into Eq. (4.57) the real and imaginary parts of the complex elasticity,  $G$ , are:

$$\frac{G_r}{E_s} = \frac{G_r^0}{E_s} - \omega_{A,D} \frac{\eta_s + \eta_s^{\text{diff}}}{E_s t_{A,D}} \frac{G_i^0}{E_s} \quad (4.62)$$

$$\frac{G_i}{E_s} = \frac{G_i^0}{E_s} + \omega_{A,D} \frac{\eta_s + \eta_s^{\text{diff}}}{E_s t_{A,D}} \frac{G_r^0}{E_s} - \omega_{A,D} \frac{\eta_s^{\text{diff}}}{E_s t_{A,D}} \quad (4.63)$$

where  $G_r^0(\omega_{A,D})$  and  $G_i^0(\omega_{A,D})$  are the real and imaginary parts of the complex elasticity calculated for a purely elastic interface, respectively [see Eq. (4.20)].

In the particular case of small frequencies,  $t_{A,D} \omega \ll 1$  (slow deformations), Eqs. (4.62) and (4.63) predict that all modules are approximately equal, i.e.  $G_r \approx G_i \approx G_r^0 \approx G_i^0 \approx E_s (t_{A,D} \omega/2)^{1/2}$ . In this case the effect of the true surface viscosity disappears, so that  $\eta_s$  cannot be measured. The numerical calculations of  $G_r$  and  $G_i$  from Eqs. (4.62) and (4.63) are illustrated in Fig. 6. The parameters are  $\eta_s^{\text{diff}}/$

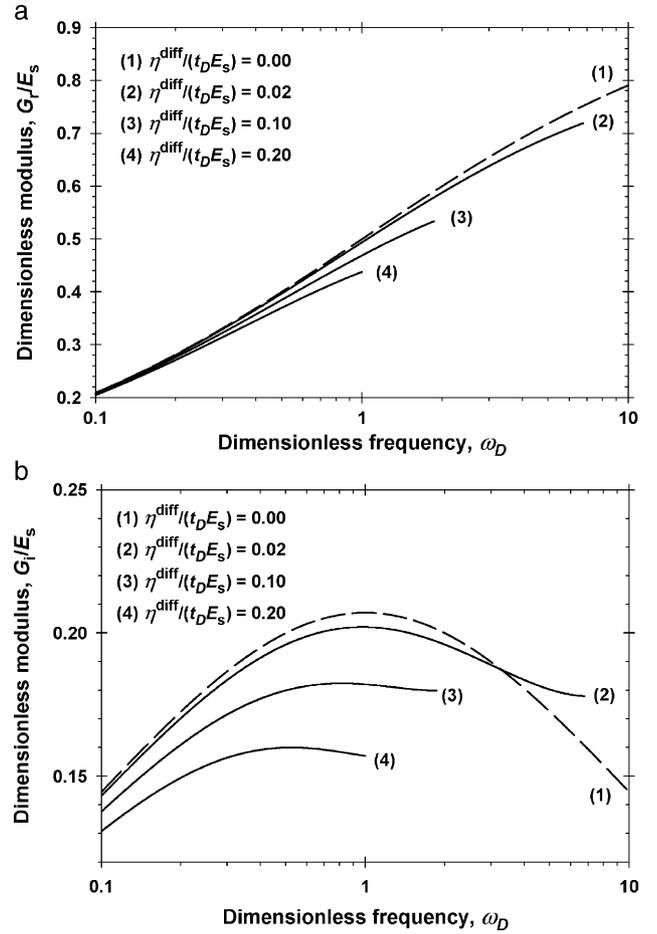


Fig. 6. Dependence of the dimensionless complex modulus,  $G_r/E_s$  (a) and  $G_i/E_s$  (b) on the dimensionless frequency,  $\omega_D = t_D \omega$  for different surface viscosities  $\eta_s^{\text{diff}}/(E_s t_D) = 2\eta_s/(E_s t_D) = 0.02, 0.1$  and  $0.2$ . The dashed line corresponds to the complex elasticity calculated from the elastic model, Eqs. (4.19) and (4.20).

( $E_s t_{A,D}) = 2\eta_s/(E_s t_{A,D}) = 0.02, 0.1$  and  $0.2$ . The dashed lines correspond to the complex elasticity modules, calculated from the model with purely elastic surface [see Eq. (4.20)]. The solid curves in Fig. 6a stop at positions, where the validity of the assumption is questionable, i.e. the frequencies are so high that the requirement  $t_r \omega \ll 1$  is not fulfilled. It is well visible that the real part of  $G$  does not change considerably (see Fig. 6a)—it becomes slightly smaller for higher surface viscosities. More interesting is the behavior of the loss modulus,  $G_i$  (see Fig. 6b). Fig. 6b shows that higher values of the surface viscosity give smaller values for the loss modulus. If the experimentalist is using for data processing the Boussinesq–Scriven constitutive law (1.12), it will give for the loss modulus,  $G_i = G_i^0 + \eta_{BS} \omega$ , i.e. the surface viscosity  $\eta_{BS}$  must increase the value of the loss modulus with respect to  $G_i^0$ , corresponding to purely elastic surface. Then the result, illustrated in Fig. 6b, which gives decrease of the loss modulus, could be interpreted as being due to a negative value of the surface viscosity,  $\eta_{BS}$ . As pointed out in the Introduction, this is not possible, since the surface viscosity must be always positive. The correct

explanation of this observation follows from Eq. (4.63) and Fig. 6a. The last two terms in the right hand side of Eq. (4.63) are roughly proportional to  $G_r^0/E_s - 1$  and since  $G_r^0/E_s \ll 1$  (see Fig. 6a), these two terms lead to negative contribution to  $G_r$ , although  $\eta_s \gg 0$ . Therefore, paradox does not exist, when correct rheological approach is used.

## 5. Concluding remarks

We have carried out a theoretical study of the phenomena, occurring at a liquid, interface covered by insoluble and soluble surfactants and subject to small dilatational perturbations. Two main processes, taking place as a result of the perturbations, are considered: surface reaction and surfactant transport onto the surface from the contiguous bulk phases. In the general case both effects lead to visco-elastic interfacial rheological behavior, while if they are both absent the surface is purely elastic.

In Section 2 we concentrated on the case of a single surface reaction in a mixture of insoluble surfactants. In this case the energy dissipation and the surface viscosity are due solely to the reaction. The adsorption  $\Gamma_k$  of the  $k$ -th component changes due both to the external perturbation (leading to a relative change of the area of the interface by  $\alpha$  with a rate  $\dot{\alpha}$ ) and to the chemical reaction, described by the change with time  $t$  of the reaction coordinate  $\xi$  [Eq. (2.10)]. The instantaneous state of the adsorbed layer is characterized by the perturbations of the adsorptions,  $\tilde{\Gamma}_k = \Gamma_k(t) - \Gamma_{k,\text{eq}}$ , where  $\Gamma_{k,\text{eq}}$  is the adsorption at equilibrium, or alternatively by the relative perturbations (called also specific deformations)  $\varepsilon_k = -\tilde{\Gamma}_k / \Gamma_{k,\text{eq}}$ . The reaction coordinate is represented as a sum of its value  $\xi_{\text{eq}}$  in the quasi-equilibrium state, corresponding to a given deformation  $\alpha$ , and a relaxation part,  $\xi_r$ , describing the deviation from this equilibrium state. The solution leads to the general visco-elastic rheological Eq. (2.24), connecting the surface stress,  $\tau_s$ , and its time derivative with  $\alpha$  and  $\dot{\alpha}$  and the parameters total surface elasticity,  $E_A$ , relaxation time of the reaction,  $t_r$ , and true surface viscosity,  $\eta_s$ . The latter is equal to the product of  $t_r$  and the reaction elasticity,  $E_r$  [see Eqs. (2.11) and (2.24)]. The reaction elasticity,  $E_r$  [see Eq. (2.21)], accounts for the change of the overall elasticity due to the transformation of the reactants into products. The general rheological Eq. (2.24) was applied to two modes of surface deformation (with constant rate,  $\dot{\alpha}$ , and periodic oscillations) and to three simple surface reactions: monomolecular transformation (which turned out to be purely elastic), dimerization and association. For fast reactions the general Eq. (2.24) transforms into Voigt equation. Maxwell equation is obtained by neglecting the terms, containing the total surface elasticity,  $E_A$ —this corresponds to fast deformation or slow reaction.

In Section 3 we have generalized the results from Section 2 to derive the constitutive rheological Eq. (3.30) of a layer consisting of a mixture of reacting soluble and insoluble surfactants. Due to the surfactant exchange with the bulk

solution the mass of the soluble components is no longer preserved and we had to replace  $\varepsilon_k$  (and  $E_k$ ) by the specific mass deformations  $\varepsilon_k^s$  (and the respective surface elasticities,  $E_k^s$ ), which account for the fact that the total mass of a given component does not change due to the reaction but only due to diffusion. The surfactant bulk diffusion fluxes,  $J_k$ , enter only implicitly in the obtained constitutive Eq. (3.30), through the terms  $\dot{\varepsilon}_k^s - \dot{\alpha}$  [see Eq. (3.16)]. Therefore, the constitutive Eq. (3.30) represents the surface stress of soluble and insoluble surfactants only through surface variables,  $\varepsilon_k^s$  and  $\alpha$ , and surface related parameters ( $E_k^s$ ,  $\eta_s$  and  $t_r$ ), i.e. the dynamic surface is described as a separate phase. In this respect Eq. (3.30) can be considered as an extension for a dynamic system with chemical reaction of the Gibbs adsorption isotherm, written in terms of the adsorption,  $\Gamma_k$ , and the surface chemical potentials,  $\mu_k^s$ , of the adsorbents:  $d\pi = \sum \Gamma_k d\mu_k^s$ . The next step (done in Section 4) of accounting in Eq. (3.30) explicitly for the mass exchange with the bulk and its effect on  $\varepsilon_k^s$  is equivalent to replacing the surface chemical potentials,  $\mu_k^s$ , in Gibbs isotherm with the respective bulk values,  $\mu_k^b$ , at adsorption equilibrium.

The considerations above lend support to our suggestion in [17,18,27] (see also the Introduction) that the viscous stress must be proportional to the rates of specific deformation rather than to the rate of total surface deformation,  $\dot{\alpha}$ , as it is often assumed. This suggestion was based on the idea (confirmed now) that the true dilatational viscous stress must include only effects due to the interaction between the adsorbed molecules and therefore, must depend on the rate of specific deformation.

The general Eq. (3.30) leads for fast reaction or slow deformation to a generalized form of Voigt Eq. (3.32), valid for soluble surfactants. Maxwell equation was obtained [see Eq. (3.35)] by neglecting in Eq. (3.30) the elastic contributions. Eq. (3.30) was also applied to two modes of deformation and to the three model reactions. It is noteworthy that for soluble surfactants the monomolecular reaction exhibits visco-elastic behavior unlike the case of insoluble surfactant.

In Section 4 attempt is made to account explicitly in the general surface rheological Eq. (4.1) for the mass transfer and its effect on the interfacial rheology. We considered first the case without surface reaction. We succeeded to show (i) that in all cases of small perturbations the surfactant flux,  $J$ , toward the surface is proportional to the surface perturbation of the adsorption,  $\tilde{\Gamma}$ , and (ii) that this always leads to a Maxwell type of Eq. (4.5) in spite of the fact that the surfaces are purely elastic. This allowed us to define appropriate surface elasticities and apparent surface viscosities,  $\eta_s^{\text{app}}$ , for oscillations of a small drop and a planar interface and continuous expansion of a drop both for diffusion controlled and barrier controlled adsorption. Analogously to the true surface viscosity,  $\eta_s$ , the apparent viscosity,  $\eta_s^{\text{app}}$ , is defined as a product of the elasticity and the characteristic time of the mass transport process. However, it is not a physicochemical property of the

interface because of its dependence on bulk parameters and the system geometry (for example on the drop radius,  $R_0$ , and the bulk diffusion coefficient,  $D$ , and for non-steady diffusion—on the frequency). One more reason for this statement is that  $\eta_s^{\text{app}}$  does not fit into the Gibbs concept of the interface as a separate phase. Finally, it does not stem from interactions between the adsorbed molecules, as the true surface viscosity,  $\eta_s$ , does.

We analyzed also the approach based on the concept of a complex surface elasticity,  $G$  [68,69]. Our analysis showed that the expressions (4.20) for the real,  $G_r$ , and imaginary,  $G_i$ , modules of  $G$  are merely convenient formulae for processing the surface tension data obtained from surface oscillations. However,  $G_i/\omega$  is not a true surface viscosity, as  $\eta_s$  (2.24), because it is due to diffusion and does not originate from interactions inside the adsorbed layer. It should not be called even “apparent surface viscosity”, because it is not defined by a self-consistent rheological relationship, such as Maxwell equation, but corresponds to Voight model, which is not applicable to purely elastic surfaces.

The analysis of the surface stress boundary condition for the drainage of a planar thin film showed, that the solution from [2] can be rearranged in such a way, that a term, proportional to the rate of deformation,  $\dot{\alpha}$ , appears, multiplied by a quantity, having dimension of surface viscosity, which we called apparent film surface viscosity,  $\eta_f^{\text{app}}$ . Again, this is not a true surface viscosity, because it is due to the surface gradients of the interfacial tension and the surfactant adsorption and therefore, it has elastic and diffusional origin. Besides, it strongly depends on the surface diffusivity,  $D_s$ , the film radius and more weakly—on the film thickness, i.e. it refers to a system of specific geometry.

The fact that  $\eta_f^{\text{app}}$  and  $G_i$  are both proportional to the Gibbs elasticity,  $E_G$ , means that there could be certain parallelism between them and the surfactant properties and concentration. Since  $\eta_f^{\text{app}}$  controls the film drainage time and thereby—the lifetime of unstable foams and emulsions, these lifetimes could also change in parallel with  $G_i$ . Indeed, the data from oscillation measurements ( $G_i$  in particular) are often used in the literature to interpret the stability of films, foams and emulsions. Such an approach suffers however from several shortcomings. To begin with, the mechanism of the two processes, film drainage and surface oscillations, is quite different. That is why they depend on different parameters: the film drainage depends on the film radius,  $R_f$ , and the surface diffusivity,  $D_s$ , which are absent from the expression for  $G_i$ ; besides,  $\eta_f^{\text{app}}$  corresponds to zero frequency,  $\omega$ , and  $G_i$  is a strong function of  $\omega$ —then the question is: at what frequency for  $G_i$  the comparison is to be made (note however that the last objection does not refer to the Expanding Drop Method, if the expansion is carried out at constant  $\dot{\alpha}$ ). Finally, while  $\eta_f^{\text{app}}$  is practically independent on the adsorption thickness  $h_a$ , the latter plays a major role for  $G_i$ , since  $\omega_D = t_D \omega$  depends on it through  $t_D = h_a^2/D$ . Since  $E_G$  increases with the surfactant concentration and  $h_a$

decreases (see Fig. 5a), the effect of  $h_a$  could in principle oppose the effect of  $E_G$  thus leading to erroneous conclusions about the efficiency of a given surfactant (see Fig. 5b).

The attempts to seek correlation between  $G_i$  and the lifetime of foams and emulsions, in cases when the thin films, preventing the coalescence of the bubbles or drops, can reach equilibrium, are even more confusing. The Gibbs elasticity can only slow down the drainage, but cannot arrest it, so that the equilibrium state of the film is entirely determined by the repulsive part of the disjoining pressure,  $\Pi$ , rather than by the Gibbs elasticity. Hence,  $G_i$  has nothing to do with this phenomenon, since the film drainage and  $G_i$  have kinetic origin and  $\Pi$  has thermodynamic nature. Therefore, these correlations have no scientific foundations. The only reason for some parallelism between  $G_i$  on the one side and film, foam and emulsion stability on the other, is the fact that both  $G_i$  (through the Gibbs elasticity) and the disjoining pressure,  $\Pi$ , are caused by the surfactant adsorption,  $\Gamma$ , and increase with it. Hence, besides originating from the adsorption, they have nothing else in common.

In the last Section 4.2 we formulated a general asymptotic procedure (and demonstrated its application on the example of the dimerization reaction), permitting to account for the coupling between the mass transfer and the surface reaction. It was supposed that the surface reaction is faster than any other process involved, i.e. that  $t_r$  is the shortest relaxation time. Using the surface deformation rate,  $\dot{\alpha} = 1/t_{\text{def}}$ , to characterize all processes besides the reaction, we showed that a small parameter  $\beta = t_r/t_{\text{def}} \ll 1$  appears. It turned out that the only non-zero term in the asymptotic expansion in terms of powers of  $\beta$  is the linear term. The application of this procedure to the general rheological equations [e.g. Eqs. (3.30) and (4.1)] lead us again to Voight type equations. It showed also that the surface reaction and the diffusion are completely decoupled, which means that the specific deformations can be obtained from the solution of the diffusion problem for the quasi-equilibrium state. We solved the respective problems for the zeroth and first approximations of  $\epsilon_s$ , which gave us Maxwell type relaxation. The respective equations for the surface stress, obtained after substituting in it  $\epsilon_s$ , has a rich rheological behavior, since it involves two models—Voight model for the basic equation and Maxwell model for the specific deformation. Depending on the values of the system parameters the overall rheological behavior could be closer to one of these models and can become predominantly elastic, visco-elastic or viscous.

In conclusion, we think that the perturbational methods (continuous expansion/contraction or oscillation) can be used (but with caution) for qualitative comparison of the efficiency of various surfactants. They can be used also for determination of  $E_G$  and  $h_a$ . We believe however that the truly new important information, which the perturbational methods can give (inaccessible by other methods to the best

of our knowledge), is on the kinetics of surface reactions and its effect on the surfactant adsorption (and related phenomena) and the surface mobility. However, the application of the theory to real systems in some cases may need generalization for parallel or consecutive surface reactions.

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