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Marangoni stresses and surface compression rheology of surfactant solutions. Achievements and problems

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ABSTRACT

In the presence of soluble surfactants, the motion of liquid surfaces involves Marangoni effects. As a consequence, the surfaces exhibit elastic responses, even frequently behaving as rigid surfaces, especially at low surfactant concentration. The Marangoni effects can be conveniently quantified introducing surface viscoelastic compression parameters that characterize the mechanical response of the surface near equilibrium. Many experimental techniques allow measuring the viscoelastic parameters. However, many difficulties are encountered during the interpretation of the surface response in the various types of hydrodynamic velocity fields involved in the different techniques. The role of adsorption and desorption energy barriers appears crucial, despite the fact that little is known yet about their values. In this short review, we will present examples illustrating the different problems.

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1. Introduction

A number of molecular species are surface-active and adsorb at the interface between water and air or a liquid immiscible in water (refereed thereafter as *oil*) [1]. Among these species, one finds small molecules made of two parts, one soluble in water and the other soluble in oil called *surfactants*. Larger molecules, such as block copolymers (including tri-block polymers of small molecular weight species such as pluronics) or comb polymers (hydrophobically grafted water soluble polymers for instance) can also be surface active. Water soluble proteins frequently unfold at liquid surfaces becoming surface-active, with their hydrophobic interiors exposed to air or oil. Particles can also adsorb at surfaces [2]: at the exception of Janus particles that have a hydrophilic and a hydrophobic side, similarly to surfactants, more common particles do not have different sides. In this case, it is the contact angle θ that determines surface activity: if θ is small or close to 180°, the particle remains either in water or in oil, but if θ is larger and not too far from 90°, particle monolayers may form.

The adsorption process decreases the surface energy, and therefore the surface tension γ, which is the surface energy per unit area. In addition, the surface becomes elastic and exerts a resistance against both compression and shear deformations [1]. When a compression is

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exerted on the surface, the surface area A occupied by the monolayer decreases and the surface tension decreases because the surface concentration Γ of surface active species increases. As a result, surface tension gradients are created between compressed and uncompressed areas: this is a *Marangoni* effect. Levich has shown in the 1940s that this effect accounted for the large damping of the surface waves on water covered by thin surface layers [3]. He also used this approach to describe the rise of bubbles in aqueous surfactant solutions, usually slower than predicted for pure water. Interestingly, the slowing down of bubbles was attributed by Boussinesq in the 1910s to the presence of a surface viscosity, but the surface viscosities are in fact too small to account for the reduction in velocity.

The Marangoni effect associated to surface concentration variation in monolayers can be quantified by a surface compression elastic modulus E. During the second half of the last century, many measurements of surface elastic and viscous parameters were performed [4]. In this review, we will briefly discuss the simple cases, and describe in more detail the cases where knowledge is still lacking or only partial. Particularly interesting is the question of how the structure of the adsorbed layer affects the adsorption dynamics and the reorganization processes present in the surface and how these determine the distribution of the Marangoni stresses appearing in the surface as a consequence of deformation. We will show examples of experiments done with different types of surfactants, proteins and/or particles.

It should be stressed that the description in terms of surface viscoelasticity, also called *surface rheology*, applies only when the monolayer is slightly perturbed. Indeed, when large perturbations are applied, the surface concentration Γ may vary appreciably, and the viscoelastic parameters are no longer constant since they depend on Γ.

2. Surface rheology

2.1. Viscoelastic parameters

Let us consider a surface compression, creating a surface tension gradient. Let us also call *surface pressure* Π the difference between the surface tensions γ_0 and γ, respectively before and after adsorption of the monolayer and follow the Levich approach [3]. The surface pressure gradient will create a force parallel to the surface displacement u_x such as $F_x = \partial\gamma/\partial x = -\partial\Pi/\partial x$, analog to the bulk force in a medium where the pressure p is not uniform. The force F_x is a Marangoni force and can be expressed in terms of the surface concentration Γ: $F_x = -(\partial\Pi/\partial\Gamma)(\partial\Gamma/\partial x)$. Assuming that the surface active species is insoluble in water, the conservation of matter in the surface implies that: $\partial\Gamma/\partial t + \Gamma\,\partial v_x/\partial x = 0$ with $v_x = \partial u_x/\partial t$. Deriving with respect to x and integrating with respect to time one gets $\partial\Gamma/\partial x = -\Gamma\partial^2 u_x/\partial x^2$ and $Fx = \Gamma\,(\partial\Pi/\partial\Gamma)(\partial^2 u_x/\partial x^2)$. The compression modulus of an insoluble monolayer is therefore:

$$E_{insol} = \Gamma\frac{\partial\Pi}{\partial\Gamma}. \tag{1}$$

For insoluble monolayers, Γ is inversely proportional to the surface area A and a more general expression can be recovered:

$$E = -A\frac{\partial\Pi}{\partial A}. \tag{2}$$

Note that the derivative in this relation may depend on the compression rate. Therefore the compression modulus can be frequency dependent in the case of periodical deformations. As in classical bulk rheology, viscosity can be introduced via a loss modulus. When the deformation is small (linear response), the loss modulus is equal to $\omega\eta_E$, η_E being the compression viscosity and ω the frequency. A complex modulus can then be also conveniently used: $\widetilde{E} = E + i\omega\eta_E$.

The most general deformation of a surface layer is, as for three dimensional systems, a combination of compression and shear [5]. When submitted to a shear deformation, the response of the monolayer is characterized by another modulus, the surface shear modulus S and another viscosity, the surface shear viscosity η_S. Most surfactant layers are fluid which makes them compliant under shear, and thus although they have a finite shear viscosity ($\eta_S \neq 0$), the shear modulus S is zero.

2.2. Soluble surfactant monolayers

When the surface layer is made of surfactants with short enough hydrocarbon chains, the surfactants are soluble in water. The surface concentration Γ is no longer known, but can be calculated from the variation of the surface tension γ with bulk surfactant concentration C, using the Gibbs equation:

$$\Gamma = -\frac{1}{k_B T}\frac{d\gamma}{d\ln C} \tag{3}$$

valid for nonionic surfactants, with k_B the Boltzmann constant, and T the absolute temperature. Expressions for ionic surfactants differ by a numerical factor, generally between 1 and 2 [1]. Note that Eq. (3) can only be used below the critical micellar concentration (*cmc*), because above this concentration, micelles form and the surface tension remains constant [6]. In general, the surface concentration Γ saturates close to the *cmc*.

Surfactant molecules may be expelled from the surface upon compression. When the molecules can exchange freely between the surface monolayer and the bulk liquid and when their motion is controlled solely by diffusion, the conservation of matter in the surface writes: $\partial\Gamma/\partial t + \Gamma\,\partial v_x/\partial x = -D\,(\partial C/\partial z)_{z=0}$, D being the surfactant diffusion coefficient in bulk. Levich [3] calculated the compression modulus in this case for a sinusoidal compression of the surface with a frequency ω:

$$E = E_{insol}\quad\frac{1+\Omega}{1+2\Omega+2\Omega^2} \tag{4}$$

with:

$$\Omega = \sqrt{\frac{D}{2\omega}}\frac{\partial C}{\partial\Gamma} \tag{5}$$

where we have employed the commonly used notations of Lucassen [7]. E is equal to E_{insol} at high frequencies, and tends to zero when ω becomes small. The characteristic relaxation time is such that $\Omega\,(\omega = 1/\tau_D) = 1$, i.e.:

$$\tau_D = \frac{2}{D}\left(\frac{\partial\Gamma}{\partial C}\right)^2. \tag{6}$$

This relaxation produces a dissipation, resulting in a contribution to the surface compression viscosity:

$$\eta_E = \frac{E_{insol}}{\omega}\frac{\Omega}{1+2\Omega+2\Omega^2}. \tag{7}$$

η_E is small if ω is either small or high and is maximum around $\omega\tau_D = 1$. This derivation does not include the intrinsic viscosity $\eta_{E,\,insol}$. It is sometimes assumed that the compression viscosity is the sum of the η_E given by Eq. (7) and of $\eta_{E,\,insol}$ [8]. This assumption leads to an inconsistency, as the viscosity should vanish when the exchanges between surface and bulk are fast compared to the time of the deformation (the surfactant does not offer resistance to this deformation). It is in fact easy to generalize the Levich derivation, for instance in the case where the relaxation inside the monolayer can be described by a single relaxation frequency k. This happens for instance when the relaxation is