

A LOCAL APPROACH IN INTERFACIAL RHEOLOGY:  
THEORY AND EXPERIMENT

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RÉSUMÉ

Une nouvelle équation constitutive pour la tension totale est proposée, en appliquant une approche locale à la dilatation d'interface des couches d'adsorption. Nous présumons que la tension visqueuse de la dilatation d'interface est proportionnée à l'augmentation relative de la surface par molécule (dilatation microscopique locale) au lieu du changement relatif de la surface totale (dilatation macroscopique) comme cela est préconisé dans la littérature. Les expériences consistant en l'expansion de la surface suivie par une relâche de tension sont menées sur le BSA (bovine serum albumin). Les résultats sont interprétés suivant l'équation rhéologique proposée ainsi que celle adoptée dans la littérature. L'élasticité d'interface et la viscosité de dilatation des couches d'adsorption du BSA obtenues avec les deux équations sont comparées.

ABSTRACT

A new constitutive equation for the total stress is proposed, applying a local approach to the interfacial dilation of adsorption layers. The interfacial dilational viscous stress is assumed to be proportional to the relative increase of the area per molecule (local microscopic dilation) instead the relative change of the total area (macroscopic dilation) as commonly adopted in the literature. Experiments consisting of surface expansion and consecutive stress relaxation are carried out with bovine serum albumin (BSA). The results are interpreted according to the proposed rheological equation as well as according to that adopted in the literature. The interfacial elasticity and dilational viscosity of BSA adsorption layers obtained by both equations are compared.

## 1/ Introduction

The deformation of an interface gives rise to stresses. The surface stresses can be represented as sums of three contributions: one stemming from the interfacial tension  $\sigma$  and two others proportional to the interfacial dilational and shear viscosities  $\eta_d$  and  $\eta_{sh}$  (1). It is usually assumed that interfacial viscous stresses are proportional to the rate of total (macroscopic) deformation (1,2). In the case of soluble surfactant, however, the observable macroscopic deformation of the interface is different from the local microscopic deformation, because of the exchange of surfactant molecules between the bulk and the interface during the deformation (see Fig.1). The main idea of our treatment is that the energy dissipation in the interfacial layer is determined by the mutual displacement of the surfactant molecules. That is why we formulate the constitutive equation in terms of local deformation (see section 2.1). We will consider the relatively simple case of radial expansion of a drop, which involves only dilational deformation.

## 2/ Theory

### 2.1/ Interfacial rheological equations

Let us consider a surface element with an area  $A$  which is extended to a new area  $A + \delta A$  for a time interval from  $t$  to  $t + \delta t$  (see Fig.1). Then the total deformation  $\alpha$  and the deformation rate  $\dot{\alpha}$  are defined as

$$\dot{\alpha} = \frac{1}{A} \frac{\delta A}{\delta t}, \quad \alpha = \int_0^t \dot{\alpha} dt \quad (1)$$

During the same time,  $\delta t$ , the adsorption of surfactant changes from  $\Gamma$  to  $\Gamma + \delta \Gamma$ . Hence, the local deformation  $\epsilon$  and the rate of the local deformation  $\dot{\epsilon}$  are defined as

$$\dot{\epsilon} = -\frac{1}{\Gamma} \frac{\delta \Gamma}{\delta t} = \frac{1}{a} \frac{\delta a}{\delta t}, \quad \epsilon = \int_0^t \dot{\epsilon} dt \quad (2)$$

where the area per molecule is  $a = 1/\Gamma$ .

It is commonly adopted in the literature that the dilational viscous stress is proportional to the rate of dilation  $\dot{\alpha}$  (1,2). Hence, one can write the basic rheological equation connecting the total stress  $\tau$  with the deformation in the form

$$\tau = G\epsilon + \eta_d \dot{\alpha} \quad (3.1)$$

where  $G$  is the surface elasticity and  $\eta_d$  is the surface dilatational viscosity. The surface viscosity, however, being a property of the adsorption layer itself, should be related to the relative displacement of the adsorbed molecules. In other words the viscous stress should be proportional to the rate of local deformation  $\dot{\epsilon}$  instead of the total one  $\dot{\alpha}$ . If this is right the basic rheological equation should read

$$\tau = G\epsilon + \eta_d \dot{\epsilon} \quad (3.2)$$

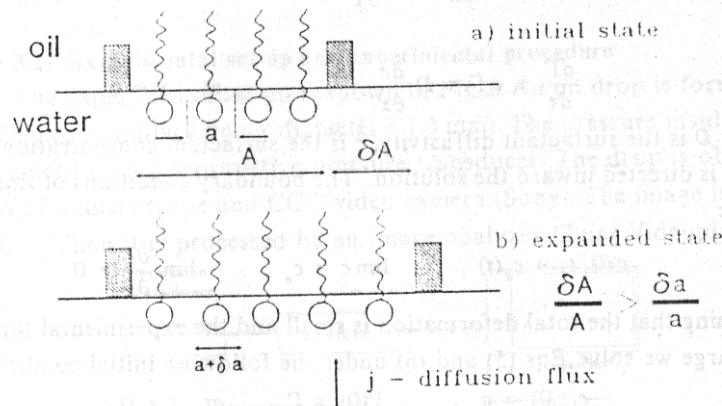


Figure 1. Expansion of a surfactant adsorption layer.

The new constitutive equation, Eq.(3.2), suggests that viscous dissipation of energy is possible even at a constant area ( $\dot{\alpha} = 0$ ) if the adsorption layer is out of equilibrium, i.e. if  $\dot{\epsilon} \neq 0$ . Hence, the adequacy of the above two constitutive equations can be verified experimentally by a stress relaxation experiment at  $\dot{\alpha} = 0$ . In contrast to  $\tau$  and  $\dot{\alpha}$ , the local deformation  $\epsilon$  and the rate of local deformation  $\dot{\epsilon}$  are not directly measurable. The latter are connected to the total (macroscopic) deformation via the mass balance equation. In order to obtain a proper expression for  $\epsilon$  and  $\dot{\epsilon}$  we solved the adsorption problem for a surface expansion and the subsequent stress relaxation due to diffusion controlled adsorption.

**2.2/ Adsorption from surfactant solutions under diffusion control during a surface expansion and a subsequent stress relaxation.**

Assuming that initially the adsorption layer rests in equilibrium with surrounding bulk phases and the perturbation of  $\Gamma$  is small, one can write

$$\Gamma(t) = \Gamma_e + \left(\frac{d\Gamma}{dc}\right)_e [c_s(t) - c_e] \quad (4)$$

where subscript  $e$  denotes equilibrium values and  $c_s$  is the subsurface surfactant concentration. The equation of the convective diffusion and the surface mass balance equation can be written in the form

$$\frac{\partial c}{\partial t} - \dot{\alpha} x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad \text{at } x > 0 \quad (5)$$

$$\frac{d\Gamma}{dt} + \dot{\alpha} \Gamma = D \frac{\partial c}{\partial x} \quad \text{at } x = 0 \quad (6)$$

where  $D$  is the surfactant diffusivity,  $c$  is the surfactant concentration and the  $x$ -axis is directed inward the solution. The boundary conditions of Eqs (4) and (5) are

$$c(0, t) = c_s(t), \quad \lim_{x \rightarrow \infty} c = c_e, \quad \lim_{x \rightarrow \infty} \frac{\partial c}{\partial x} = 0 \quad (7)$$

Assuming that the total deformation is small and the experimental time is not very large we solve Eqs (5) and (6) under the following initial conditions

$$c(x, 0) = c_e, \quad \Gamma(0) = \Gamma_e \quad \text{at } t = 0 \quad (8)$$

The final solutions for  $\epsilon$  and  $\dot{\epsilon}$  are

$$\epsilon = \int_0^{t_A^{(t)}} \exp\left[-\frac{t_A^{(t)} - \hat{t}}{t_D}\right] \operatorname{erfc}\left[\sqrt{\frac{t_A^{(t)} - \hat{t}}{t_D}}\right] \frac{d}{d\hat{t}} \left(\frac{A}{A_0} - 1\right) d\hat{t} \quad (9)$$

$$\dot{\epsilon} = \left(\frac{A}{A_0}\right)^2 \left[ \frac{d}{dt_A} \left(\frac{A}{A_0} - 1\right) + \frac{\epsilon}{t_D} - \frac{1}{t_D \sqrt{\pi}} \int_0^{t_A^{(t)}} \sqrt{\frac{t_D}{t_A^{(t)} - \hat{t}}} \frac{d}{d\hat{t}} \left(\frac{A}{A_0} - 1\right) d\hat{t} \right] \quad (10)$$

where

$$t_A^{(t)} = \int_0^t \left(\frac{A}{A_0}\right)^2 d\hat{t} \quad \text{and} \quad t_D = \frac{1}{D} \left(\frac{d\Gamma}{dc}\right)_e^2 \quad (11)$$

are the normalized time and the characteristic diffusion time respectively.

### 3/ Experiments

#### 3.1/ Materials and methods

We performed experiments with Bovine Serum Albumin (BSA, Sigma, 98-99%) adsorption layers at the n-decane/water interface. The BSA concentration and the ionic strength were kept constant, while the pH was varied from  $\sim 5$  to  $\sim 8$ . Sodium chloride was added to adjust the ionic strength.

We used a method based on the simultaneous measurement of the capillary pressure  $P_c$  and the radius  $R$  of an oil drop immersed into a surfactant solution. Knowing these parameters one can calculate the stress  $\tau$  and the drop area  $A$  during the expansion ( $\dot{\alpha} > 0$ ) and the stress relaxation ( $A = \text{const}$ ,  $\dot{\alpha} = 0$ ).

#### 3.2/ Experimental set-up and experimental procedure

The experimental set-up is shown in Fig.2. An oil drop is formed at the tip of a glass capillary (inner diameter = 1.3 mm). The pressure inside the drop is measured by a piezoresistive pressure transducer. The drop is observed by means of a microscope and CCD video camera (Sony). The image is recorded by VCR. Then it is processed by an image analyzer (Zeiss Videoplan 2).

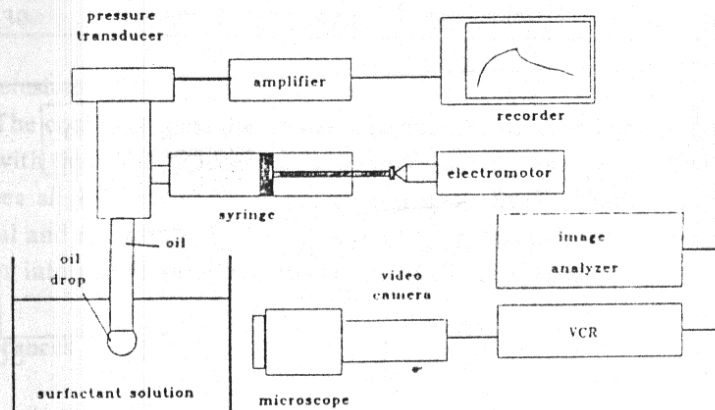


Figure 2. Sketch of the experimental set-up.

The investigated expansion - relaxation experiment can be divided in three stages: (i) an initial formation of a saturated BSA adsorption layer at the oil/water interface keeping the drop area constant for about 4 hours, (ii) an expansion of the adsorption layer increasing the drop area for  $\sim 10$  seconds and (iii) a relaxation of the expanded adsorption layer under a constant drop area. The drop radius  $R$  and the drop height  $H$  were measured from the video-

records. Then the area  $A$  and the rate of total deformation were calculated by the formulae

$$A = 2\pi RH, \quad \dot{\alpha} = \frac{d \ln A}{dt} \quad (12)$$

The total stress  $\tau$  was calculated by using the equation

$$\tau = \frac{1}{2} [P_c(t) R(t) - P_c(0) R(0)] \quad (13)$$

which stems from Laplace equation of capillarity;  $P_c(0)$  and  $R(0)$  are the initial values of the capillary pressure and the drop radius, whereas  $P_c(t)$  and  $R(t)$  are their values at a subsequent moment  $t$ .

#### 4/ Results and discussion

A typical curve of the total tension,  $\tau$ , vs time is shown in Fig.3. One can see that during the expansion  $\tau$  sharply increases and reaches a maximum value just at the end of expansion. Then  $\tau$  gradually decreases due to the adsorption of BSA molecules on the oil/water interface at a constant drop area.

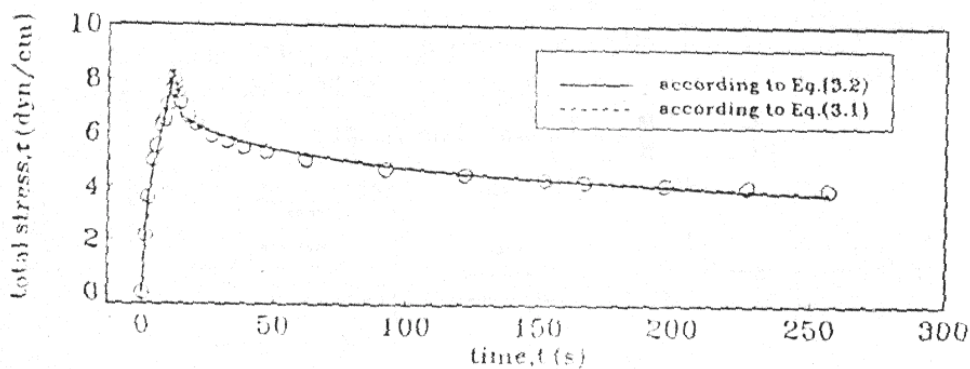


Figure 3. A typical curve of the total stress vs time.  $C_{BSA} = 0.0125\text{wt}\%$ , ionic strength 0.2 M,  $T = 22.4^\circ\text{C}$ ,  $\text{pH} = 8.3$ .

Both Eq.(3.1) and Eq.(3.2) provide a good fit of the experimental data. The values for the surface rheological parameters calculated by means of these two equations are compared in Table 1. Both equations give almost identical values for  $G$ ,  $\eta_s$  and  $\epsilon_p$ . The root mean square deviations (RMSD) are small, but a little higher for Eq.(3.1). This suggests that the two models might be distinguished under proper conditions. The elasticity does not change

appreciably with pH and is equal to  $\sim 19$  dyn/cm. The measured value of the *dilatational* elasticity  $G$  is close to the values obtained by Graham and Phillips for the surface *shear* elasticity at petroleum ether/ water interface (3). The interfacial viscosities obtained by us, however, are about 10 times lower from those determined in Ref.(3) and do not change very much with pH. This discrepancy might be attributed to the two times higher ionic strength in our experiments.

Finally, we would like to emphasize that the proposed theory deals with the case of diffusion controlled adsorption. The adsorption of BSA, however, can be more complicated (4,5).

**Table 1.** Rheological properties of BSA adsorption layers at n-decane/water interface obtained according to Eq.(3.2) and Eq.(3.1) (given in parentheses). Ionic strength,  $i = 0.2$  M;  $C_{BSA} = 0.0125$  wt%;  $T = 22.4^\circ\text{C}$ .

pH	$G$ (dyn/cm)	$\eta_d$ (dyn.s/cm)	$t_D$ (s)	RMSD(dyn/cm)
5.05	18.2 (17.8)	56.5 (57.4)	281 (281)	0.179 (0.202)
5.98	18.6 (18.6)	76.2 (80.4)	569 (569)	0.286 (0.372)
8.30	18.7 (18.9)	75.0 (67.4)	760 (760)	0.200 (0.242)

### 5/ Conclusions

The comparison of the new rheological constitutive equation, proposed by us, with that usually accepted in the literature shows, that the new equation describes slightly better the experimental data. Both equations give almost identical and realistic values for  $G$ ,  $\eta_d$  and  $t_D$  of the studied system and can be used for interpretation of expansion - relaxation experiments.

### 6/ References

1. L.E.Scriven (1960) *Chem. Eng. Sci.*, **12**, 98.
2. D.A.Edwards, H.Brenner, and D.T.Wasan (1991) *Interfacial Transport Processes and Rheology*, Butterworth-Heinemann, U.S.A., Ch.4.
3. D.E.Graham, and M.C.Phillips (1980) *J. Colloid Interface Sci.*, **76**, 240.
4. D.E.Graham, and M.C.Phillips (1979) *J. Colloid Interface Sci.*, **70**, 415.
5. A.J.I.Ward, and L.H.Regan (1980) *J. Colloid Interface Sci.*, **78**, 389.