

Dynamic surface properties of aqueous Brij58 solutions at the air/water interface

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Abstract

For surfactant Brij58, which exhibits the dynamic characteristic of slow diffusion-controlled adsorption at the air/water interface, the stress relaxation method was used to measure the Gibbs elastic modulus (ϵ_0) and the diffusion relaxation time (τ_D). Two other methods, the peak tensiometric method proposed recently by M. Van Uffelen and P. Joos and a strip method, were also used to obtain $\epsilon_0\sqrt{\tau_D}$ as a comparison. The three methods give consistent results. A discussion is presented of the description of the dynamic parameters by the Langmuir and Freundlich isotherms which fit the equilibrium surface tension concentration curve reasonably well. The Langmuir isotherm gives erroneous results for ϵ_0 and τ_D but the correct order of magnitude for $\epsilon_0\sqrt{\tau_D}$. The Freundlich isotherm can better describe ϵ_0 and τ_D but gives a poorer result for $\epsilon_0\sqrt{\tau_D}$ than the Langmuir isotherm.

Keywords: Brij58; Diffusion relaxation time; Dynamic surface properties; Gibbs elastic modulus

1. Introduction

The dynamic surface properties of a surfactant system are expressed by a complex modulus of elasticity $\epsilon(i\omega)$. For a diffusion-controlled adsorption process of a single component system, this modulus is given by the well-known relationship [1]

$$\epsilon(i\omega) = \epsilon_0 \frac{1 + \left(\frac{\omega_0}{2\omega}\right)^{1/2} + i \left(\frac{\omega_0}{2\omega}\right)^{1/2}}{1 + 2 \left(\frac{\omega_0}{2\omega}\right)^{1/2} + 2 \left(\frac{\omega_0}{2\omega}\right)} \quad (1)$$

where ω is the radial frequency, ϵ_0 is the thermo-

dynamic or Gibbs elasticity given by $\epsilon_0 = -d\sigma/d(\ln \Gamma)$ (where σ is the surface tension and Γ is the adsorption), and ω_0 is the relaxation frequency given by $\omega_0 = D(dC/d\Gamma)^2 = 1/\tau_D$ (where D is the diffusion coefficient, C is concentration and τ_D is the diffusion relaxation time).

These dynamic surface properties can be obtained in principle from equilibrium surface tension measurements using a suitable equation of state (ideal surface behaviour, regular surface behaviour [1], Temkin isotherm [2], Freundlich isotherm [3], etc.), but it appears [3,4] that although the equilibrium properties are reasonably well described by one of these isotherms, the dynamic properties ϵ_0 and $d\Gamma/dC$ are very sensitive to the choice of this isotherm. The results presented in this paper may be an illustration of this. Hence

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it seems better to obtain these properties by direct measurement. Several techniques are now available for obtaining the modulus of elasticity, e.g. the longitudinal wave technique [5], the damping of capillary waves [6], the oscillating bubble [7] and laser beat spectroscopy [8].

In this paper these properties are obtained using a somewhat different approach, restricted to slowly adsorbing surfactant solutions, with adsorption relaxation times of more than 1 s.

2. Theory

Recently Van Uffelen and Joos [9] have proposed the peak tensiometric method for measuring dynamic surface properties of surfactant systems. Here an equilibrium surfactant surface in a Langmuir trough is linearly expanded, and the surface tension is recorded. It is seen that initially the surface tension increases, goes through a maximum and decreases slowly. If at time $t=0$, the area of the surfactant surface is Ω_0 and the area expands with a constant rate ($d\Omega/dt = \text{constant}$, where Ω is the area of the surface and t is time) we can define a constant α :

$$\alpha = \frac{1}{\Omega_0} \frac{d\Omega}{dt} \quad (2)$$

and the area of the surface with time is

$$\Omega = \Omega_0(1 + \alpha t) \quad (3)$$

The corresponding jump in surface tension $\Delta\sigma$, being the surface tension at a time $t(\sigma)$ minus the equilibrium surface tension (σ_e), i.e. $\Delta\sigma = \sigma - \sigma_e$, is given by the following equation for a diffusion-controlled adsorption process for a single surfactant system:

$$\Delta\sigma = \frac{\epsilon_0 x}{1+x} \left[\frac{1}{1 + \left(\frac{4x}{3\pi\alpha\tau_D} \right)^{1/2} \left(\frac{x^2 + 3x + 3}{x^2 + 2x + 1} \right)^{1/2}} \right] \quad (4)$$

where $x = \alpha t$. In all the experiments that we have carried out until now, except for a very small

period of time after starting the experiment

$$1 \ll \left(\frac{4x}{3\pi\alpha\tau_D} \right)^{1/2} \left(\frac{x^2 + 3x + 3}{x^2 + 2x + 1} \right)^{1/2}$$

and Eq. (4) reduces to

$$\Delta\sigma = \epsilon_0 \sqrt{\tau_D} \left(\frac{3\pi\alpha}{4} \right)^{1/2} \left(\frac{x}{x^2 + 3x + 3} \right)^{1/2} \quad (5)$$

and it is seen that a maximum is obtained for $x = \sqrt{3}$ and the corresponding peak in the surface tension is

$$\Delta\sigma = 0.604\epsilon_0 \sqrt{\tau_D} \sqrt{\alpha} \quad (6)$$

Hence by performing experiments with different values of α and plotting $\Delta\sigma_p$ (the jump in surface tension at the peak) as a function of $\sqrt{\alpha}$ we obtain $\epsilon_0 \sqrt{\tau_D}$ from the slope. Using the Gibbs equation it is seen that

$$\epsilon_0 \sqrt{\tau_D} = \frac{RT\Gamma^2}{C_0 \sqrt{D}} \quad (7)$$

where C_0 is the bulk concentration. The product $\epsilon_0 \sqrt{\tau_D}$ can also be obtained using other techniques, e.g. by expanding the surface with a constant dilation rate $\theta (= d \ln \Omega / dt)$, as was done by Van Voorst Vader et al. [10], or by our strip method [11], or by using the long-time approximation for the relaxation of the dynamic surface tension [12] (for example, the inclined plate method [13], the oscillating jet [14] and the maximum bubble pressure method [15]). With these techniques, measurements are possible in a small time domain (a few milliseconds and larger). Alternatives for the peak tensiometric method are the growing drop techniques introduced by MacLeod and Radke [16].

As a conclusion the parameter $\epsilon_0 \sqrt{\tau_D}$ can be obtained in a very broad time domain, but some other technique is needed to obtain ϵ_0 and/or τ_D .

For a slowly adsorbing surfactant system, ϵ_0 and τ_D can be measured with the stress relaxation technique, proposed among others by Loglio et al. [17]. Here an equilibrated surface of a surfactant system is suddenly expanded or compressed from an area Ω_0 until an area Ω is reached. In principle the expansion or compression must be a step

function; in practice the expansion or compression time must be much less than the diffusion relaxation time. For this experiment and for small jumps in surface tension, the relaxation to equilibrium is given by the Sutherland equation [18]:

$$\Delta\sigma = \Delta\sigma_0 \exp\left(-\frac{t}{\tau_D}\right) \operatorname{erfc} \sqrt{\frac{t}{\tau_D}} \quad (8)$$

where $\Delta\sigma_0$ is the initial jump in surface tension at $t = 0$; $\Delta\sigma_0 = \sigma_0 - \sigma_e$ (where σ_0 is the surface tension jump after the stepwise surface deformation). For small jumps, $\Delta\sigma_0$ is related to the Gibbs elasticity by

$$\Delta\sigma_0 = \epsilon_0 \frac{\Omega - \Omega_0}{\Omega_0} \quad (9)$$

Hence by means of the stress relaxation experiment, both ϵ_0 and τ_D are obtained separately. The method of peak tensiometry is used to obtain $\epsilon_0\sqrt{\tau_D}$ as a check. The resulting parameters ϵ_0 , τ_D and $\epsilon_0\sqrt{\tau_D}$ are compared with data obtained from the equilibrium surface tension concentration curve. It will be seen that large discrepancies are obtained.

3. Experiment

The surfactant Brij58 was a sample obtained from Serva. It is a non-ionic surfactant with the chemical formula $\text{CH}_3-(\text{CH}_2)_{15}-(\text{OCH}_2-\text{CH}_2)_n-\text{OH}$ (where $n = 20$). Milli-Q water was used thoroughly, and care was taken concerning the usual cleanliness of the glassware and the apparatus. The equilibrium surface tension concentration curve did not show a minimum at the CMC. Although our Brij58 sample is not pure, possible contaminants are not highly surface active and should have, if any, minor effects on the equilibrium and dynamic properties.

Stress relaxation [19] and strip [11] experiments were performed as described previously. Peak tensiograms were also obtained as described before [9], but great care was taken regarding the

avoidance of leakage of solution around the barrier. This aspect will be considered separately [20].

4. Results

In Fig. 1, typical peak tensiograms are presented. For similar tensiograms, the jumps in surface tension at the peak, $\Delta\sigma_p$, are plotted as a function of $\sqrt{\alpha}$ (see Fig. 2) giving $\epsilon_0\sqrt{\tau_D}$ from the slopes. The

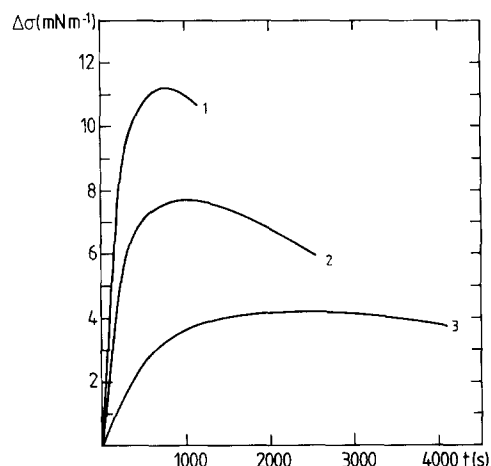


Fig. 1. The jump in surface tension as a function of time for the linearly expanded surface of aqueous Brij58 solution ($C = 1.25 \times 10^{-9} \text{ mol cm}^{-3}$): curve 1, $\alpha = 0.0379$; curve 2, $\alpha = 0.0156$; curve 3, $\alpha = 0.00517$.

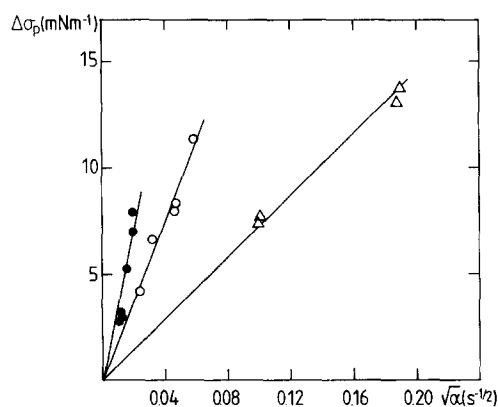


Fig. 2. The jump in surface tension at the peak vs. $\sqrt{\alpha}$: ●, $C = 1.25 \times 10^{-9} \text{ mol cm}^{-3}$; ○, $C = 2.5 \times 10^{-9} \text{ mol cm}^{-3}$; △, $C = 7.52 \times 10^{-9} \text{ mol cm}^{-3}$.

results for three different concentrations are given in Table 1.

In Fig. 3, typical results of the stress relaxation experiment are given. The results for the Gibbs elasticity and the diffusion relaxation time are given in Table 2 for different concentrations.

In Fig. 4, we have plotted $\epsilon_0\sqrt{\tau_D}$ as a function of concentration obtained by the different methods.

Table 1
Peak tensiometry for Brij58 solution at three different concentrations

$10^9 C$ (mol cm ⁻³)	$\epsilon_0\sqrt{\tau_D}$ (mN m ⁻¹ s ^{1/2})
1.25	504.9
2.50	295.6
7.52	112.3

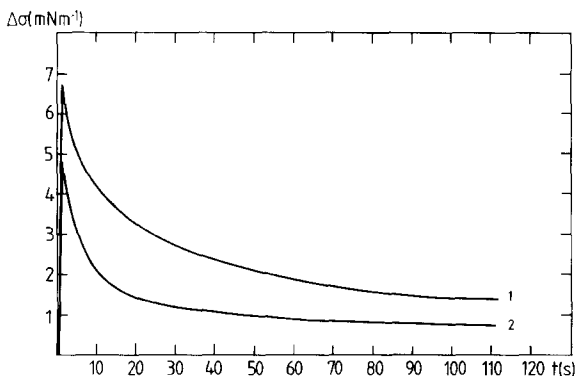


Fig. 3. The jump in surface tension as a function of time for the stress relaxation experiment: curve 1, $C = 5 \times 10^{-9}$ mol cm⁻³; curve 2, $C = 1 \times 10^{-8}$ mol cm⁻³.

Table 2
Gibbs elasticity and diffusion relaxation time for different Brij58 solutions

C (mol cm ⁻³)	ϵ_0 (mN m ⁻¹)	τ_D (s)	$\epsilon_0\sqrt{\tau_D}$ (mN m ⁻¹ s ^{1/2})
5×10^{-10}	15.5	1200.3	537.0
1×10^{-9}	20.8	525.0	476.0
2×10^{-9}	26.7	202.6	380.0
3×10^{-9}	28.5	75.0	246.8
5×10^{-9}	32.0	22.1	150.4
7×10^{-9}	29.5	15.0	114.3
1×10^{-8}	26.6	9.0	79.8

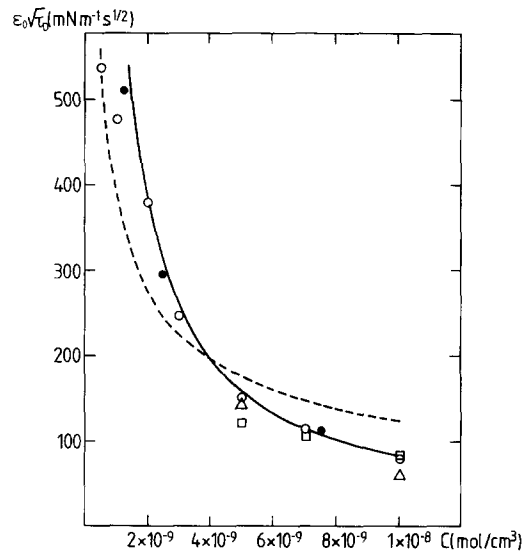


Fig. 4. $\epsilon_0\sqrt{\tau_D}$ as a function of concentration: \circ , Stress relaxation method; \triangle , Van Hunsel [21]; \bullet , peak tensiometric method; \square , strip method; —, from the Langmuir equation; ---, from the Freundlich equation.

It is seen that the peak tensiometric method and the stress relaxation method give consistent results.

The results obtained by the strip method are somewhat low, especially for low concentrations.

Finally, in Fig. 5 the equilibrium surface tension is presented.

5. Discussion

The equilibrium surface tension concentration curve fits the von Szyszkowski equation [21] reasonably well:

$$\sigma = \sigma_w - RT\Gamma^\infty \ln\left(1 + \frac{C}{a}\right) \quad (10)$$

where σ_w is the surface tension of water, Γ^∞ is the saturation adsorption (2.7×10^{-10} mol cm⁻²), and a is the Langmuir–von Szyszkowski constant (6.2×10^{-11} mol cm⁻³).

The saturation adsorption was obtained from the equilibrium surface tension concentration curve at $C = 10^{-8}$ mol cm⁻³, using the Gibbs adsorption equation.

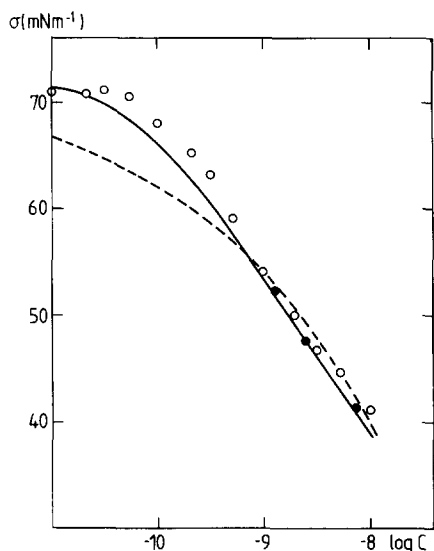


Fig. 5. Equilibrium surface tension for aqueous Brij58 solution as a function of concentration (mol cm⁻³): ○, Van Hunsel [21]; ●, Horozov [20]; —, Langmuir equation; and ---, Freundlich equation.

The use of a regular surface behaviour gives a somewhat better fit:

$$\sigma = \sigma_w + RT\Gamma^\infty \ln\left(1 - \frac{\Gamma}{\Gamma^\infty}\right) + RT\Gamma^\infty H \left(\frac{\Gamma}{\Gamma^\infty}\right)^2 \quad (11)$$

$$C = \frac{a\Gamma}{\Gamma^\infty - \Gamma} \exp\left[H\left(1 - \frac{2\Gamma}{\Gamma^\infty}\right)\right]$$

Using the Langmuir isotherm (which is related to the von Szyszkowski equation by the Gibbs equation) gives for the Gibbs elasticity:

$$\epsilon_0 = RT\Gamma^\infty \frac{C}{a} \quad (12)$$

However, the values coming out of this are far too high compared with the data given in Table 2. For example, for $C = 1.0 \times 10^{-8}$ mol cm⁻³, we found experimentally, $\epsilon_0 = 26$ mN m⁻¹, whereas the calculated value from Eq. (12) gives $\epsilon_0 = 1085$ mN m⁻¹, higher by a factor of 40.

Similarly, using the Langmuir equation we obtain

$$\frac{d\Gamma}{dC} = \frac{\Gamma^\infty a}{(a + C)^2} \quad (13)$$

This value is also obtained from the diffusion relaxation time using a diffusion coefficient $D = 5 \times 10^{-6}$ cm² s⁻¹. The results are given in Fig. 6 and are quite different from the experimental data.

However, although the equilibrium surface tensions are quite reasonably described by the von Szyszkowski equation, the dynamic data calculated from them are erroneous. However, we can also describe $\epsilon_0\sqrt{\tau_D}$ by the Langmuir model, giving

$$\epsilon_0\sqrt{\tau_D} = \frac{RT(\Gamma^\infty)^2}{\sqrt{D}} \frac{C}{(a + C)^2} \quad (14)$$

(with $D = 5 \times 10^{-6}$ cm² s⁻¹).

The comparison is made in Fig. 4, and it is seen that the experimental results are more or less described by Eq. (14); hence the errors in ϵ_0 and $d\Gamma/dC$ cancel each other more or less. In some way this is understandable. In Eq. (14) adsorption is involved and is obtained from the derivative of the σ - C curve, whereas for obtaining ϵ_0 and $d\Gamma/dC$, a second derivative is needed and seems to be very imprecise. Rearranging in Fig. 7, the experimental adsorption obtained from Eq. (7) is compared with the results from the Langmuir equation and some

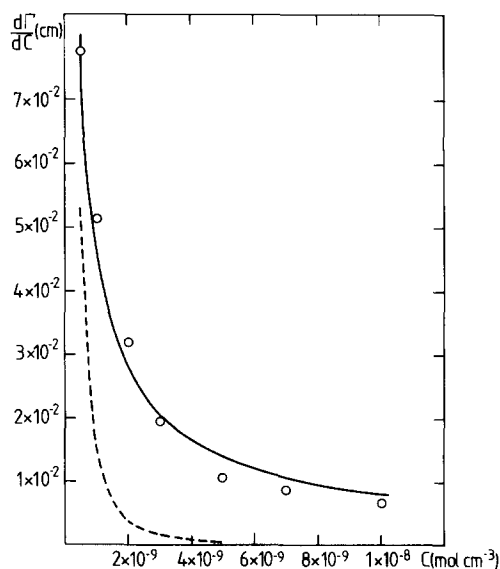


Fig. 6. $d\Gamma/dC$ as a function of concentration: ○, from the stress relaxation experiment; —, from the Freundlich equation; ---, from the Langmuir equation.

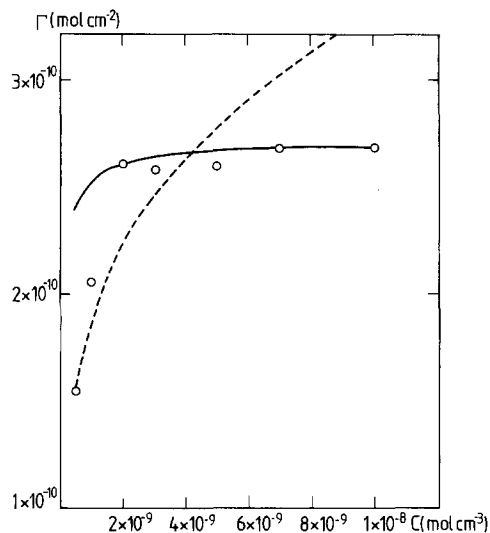


Fig. 7. Adsorption as a function of concentration: \circ , obtained from dynamic parameters; —, from the Langmuir equation; ---, from the Freundlich equation.

agreement is obtained; certainly the order of magnitude seems correct.

Some workers [3] prefer to use the Freundlich isotherm

$$\Gamma = KC^n \quad (15)$$

The Freundlich isotherm is only an empirical description since for $C \rightarrow \infty$, $\Gamma \rightarrow \infty$ which is not consistent with the saturation adsorption Γ^∞ . The equilibrium surface tension data (see Fig. 5) are, in the concentration range considered, described by the equation

$$\sigma = \sigma_w - \frac{RTK}{n} C^n \quad (16)$$

where $K = 3.32 \times 10^{-8}$ and $n = 0.25$.

From this we obtain for the Gibbs elasticity

$$\epsilon_0 = \frac{RTK}{n} C^n \quad (17)$$

and in Fig. 8 a comparison is made between the experimental data and those calculated by means of Eq. (17); it is seen that some agreement is obtained. Similarly, we performed comparisons in Figs. 4, 6 and 7 for the other parameters ($\epsilon_0 \sqrt{\tau_D}$,

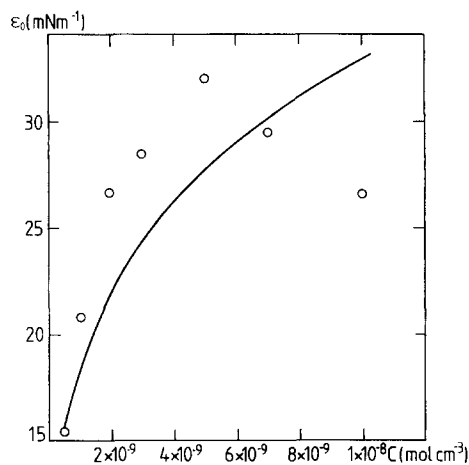


Fig. 8. Gibbs elastic modulus as a function of concentration: \circ , stress relaxation experiment; —, from the Freundlich equation.

$d\Gamma/dC$ and Γ). Here $d\Gamma/dC$ is given by

$$\frac{d\Gamma}{dC} = nKC^{n-1} \quad (18)$$

We can conclude that the equilibrium surface tension concentration curve is described better by the Langmuir equation than by the Freundlich isotherm, which is inappropriate for small concentrations. The value of $\epsilon_0 \sqrt{\tau_D}$ is also better described by the Langmuir isotherm instead of the Freundlich isotherm; perhaps the same is true for the adsorption. However, the Langmuir isotherm gives erroneous results for the Gibbs elasticity ϵ_0 and the diffusion relaxation time. The Freundlich isotherm gives somewhat better data. Hence it seems rather dangerous to obtain parameters for the dynamic surface properties from an equilibrium surface tension concentration curve.

Another point of interest is that the modulus of elasticity attains a maximum (Fig. 8). This is rather unexpected. Since at present no surface equation of state is available, we are unable to give an explanation for this. We have to accept this as an experimental fact.

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