

Effect of the polydispersity of diffusing micelles on the surface elasticity

C.D. Dushkin¹ and I.B. Ivanov

Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

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Abstract

The effect of the polydispersity of the micelles on the surface elasticity modulus of surfactant solutions subjected to periodical oscillations is studied theoretically. By using the results of a previous theoretical study (C.D. Dushkin, I.B. Ivanov and P.A. Kralchevsky, *Colloids Surfaces*, 60 (1991) 235) two important cases of surfactant diffusion are considered.

First, diffusion affected by the slow relaxation process of micellization. Expressions for the elasticity modulus and its oscillation-retarding phase are derived. They appear as a special case of the equations of Lucassen for monodisperse micelles (J. Lucassen, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 76). The parameters of the micelle size distribution (mean aggregation number and dispersion) are computed from the data of Lucassen. The values of the calculated parameters are in agreement with their experimental values for different surfactants, obtained by chemical relaxation techniques.

Second, diffusion affected by the fast relaxation process of micellization. The equations for the surface elasticity modulus derived here cannot be obtained in the frame of Lucassen's model because the fast relaxation process is a net result of the polydispersity of the micelles. In both cases, the micelles enhance the exchange of monomers between the adsorption layer and the solution. Hence, the effective viscous behavior of the adsorption layer becomes more pronounced.

1. INTRODUCTION

The surface rheological properties of the surfactant layers are important for foam or emulsion stability. The interactions between the bubbles or droplets in these systems are accompanied by an unstoppable deformation and expansion of the adsorption layers. Their ability to resist the disturbances is determined by two factors. One of these is represented by the surface shear and dilational viscosities, which are counterparts of the respective bulk quantities. They account for the interactions between the adsorbed molecules and are probably of minor

¹To whom correspondence should be addressed.

importance in the case of the soluble low molecular weight surfactants which we consider here. The second factor is the surface apparent viscosity, which has no bulk analog. This apparent viscosity is due to the exchange of surfactant molecules between the adsorption layer and the solution.

The apparent surface viscosity is connected with the surface dilational modulus, E , determining the viscoelastic behavior of the adsorption layer. It gives the change in the surface tension, σ , corresponding to the alteration of the area A of the adsorption layer

$$E = d\sigma/d(\ln A) \quad (1.1)$$

The dilational modulus depends on the way the experiment is performed. There are a number of experiments for measuring E , originating chiefly from Ref. [1]. The adsorption layer can be subjected to periodic oscillations of different frequencies: around 1 Hz in the method of oscillating barriers [2,3]; 100 Hz in the longitudinal waves method [4,5]; 10^4 Hz in the method of capillary waves produced by thermal interfacial fluctuations [6,7]. The area of the adsorption layer can be changed continuously, or with a jump, in a Langmuir trough [1,8] or in a funnel [9]. Furthermore, the relaxation of the surface tension is usually measured by a Wilhelmy plate or by light scattering [6,7].

The dilational modulus E is a complex quantity which may be represented as [10]

$$E = E_R + iE_I = |E| \exp(i\psi) \quad (1.2)$$

where $i^2 = -1$. The real part, E_R , gives the elastic energy stored in the adsorption layer while the imaginary part, E_I , accounts for the energy dissipated in the layer during the oscillations. The dissipation is due to the apparent surface viscosity, i.e. to the exchange of surfactant with the adjacent solution. Hence, by studying the dependence $E(\omega)$ one obtains information about the viscoelasticity of the adsorption layer.

The absolute value $|E|$ and the phase ψ of the modulus

$$|E| = (E_R^2 + E_I^2)^{1/2} \quad \psi = \arctan(E_I/E_R) \quad (1.3)$$

can be measured directly. When the adsorption layer has purely elastic behavior ($E_I = 0$) the surface tension changes in proportion to the surface area. The exchange of surfactant molecules between the bulk and the interface is negligible. In the case of viscoelastic behavior ($E_I > 0$) a phase difference between the variations of the surface tension and surface area arises. The mass transfer exhibits a tendency to reduce the deviations of the surface tension from equilibrium. That is why in this case the dilational modulus also depends on the way the surfactant

molecules are transported to the interface. Here we shall consider the case of diffusion control, i.e. the case when the diffusion mass transfer from the bulk to the subsurface layer is much slower than the adsorption of molecules onto the surface. The opposite case of slow adsorption is reviewed in Ref. [10].

We shall restrict our considerations to the experiments of Lucassen and co-workers [2,3,11]. The sinusoidal perturbations in the surfactant layer adsorbed on the surface of water solutions are produced by two moving barriers. They oscillate with a small amplitude (relative deviation $|\Delta A/A| \approx 0.06$) and a frequency of 0.05–10 cps (angular velocity $\omega \approx 0.0052\text{--}1.047\text{ s}^{-1}$). The compression and expansion of the layer are uniform over the whole area between the barriers. The respective variations of the surface tension ($\Delta\sigma \approx 0.1\text{--}4\text{ dyn cm}^{-1}$) are monitored by the Wilhelmy plate method. Lucassen and van den Tempel [2] have developed a theory which relates E to the parameters of the surfactant solution at concentrations below the critical micelle concentration (CMC). They have solved the diffusion problem at appropriate boundary conditions. To do this they have assumed that the deviations of the adsorption, surface tension and bulk surfactant concentration from their equilibrium values are small. In such a way Lucassen and van den Tempel have obtained an expression for E and have calculated the parameters of the adsorption isotherm of decanoic acid from the experimental data for $|E|$ and ψ .

Lucassen later generalized the theory for surfactant concentrations above the CMC [11]. To account for the effect of the micelles he has supposed that: (i) only one sort of micelle containing m monomers is present in the solution; (ii) the monodisperse micelles can move due to diffusion but they do not adsorb onto the surface; and (iii) the micellization kinetics can be described by a one-step reaction mechanism when one micelle disintegrates directly to m monomers. The main conclusion of this theory is that the micelles do affect the surface elasticity by enhancing the exchange of material between the adsorption layer and the solution (for more details see below). By using this theory Lucassen has calculated the characteristic micellization time from the experimental data for several surfactants. This is the first attempt to study the micellization kinetics in the bulk of solution by means of surface experimental methods.

In reality the micelles are polydisperse particles. The micellar solution contains aggregates, which consist of a variable number of surfactant molecules (monomers) s . The abundant micelles with $s > s_2$ have a gaussian size distribution. The transition size region ($s_1 < s \leq s_2$), where the rare aggregates are placed, connects the micellar region with the oligomer region ($1 \leq s \leq s_1$). This complex system has a

peculiar behavior in non-equilibrium conditions. It is known that the kinetics of micellization at small deviations from equilibrium are connected with two relaxation processes, fast and slow, whose time constants, τ_F and τ_{SL} , differ appreciably [12–15]. For example, in the stopped-flow experiment [12] the micelles transform during the fast relaxation into smaller ones, thus lowering their mean aggregation number. However, the total concentration of the micelles remains nearly constant. During the slow relaxation the mean aggregation number increases to its initial value. The micelles decrease in number until the new equilibrium concentration is reached.

Aniansson and co-workers [13–15] have obtained expressions for τ_F and τ_{SL} , dependent on the parameters of the micellar system. The relaxation time of the fast process is

$$\tau_F = \left[\frac{k_m^-}{\sigma_m^2} (1 + \sigma_m^2 \beta_m) \right]^{-1} \quad (1.4)$$

and of the slow process:

$$\tau_{SL} = \left(\frac{1}{R \bar{c}_1 \beta_m} \frac{n_2 \beta_n + m_2 \beta_m}{n_2 \beta_n + \sigma_m^2 \beta_m} \right)^{-1} \quad (1.5)$$

The constants in Eqns (1.4) and (1.5) are defined as follows:

$$m = \sum_{s_2+1}^{s_3} s \bar{c}_s / \bar{c}_m \quad m_2 = m^2 + \sigma_m^2 = \sum_{s_2+1}^{s_3} s^2 \bar{c}_s / \bar{c}_m \quad (1.6a)$$

$$n = \sum_1^{s_1} s \bar{c}_s / \bar{c}_n \quad n_2 = n^2 + \sigma_n^2 = \sum_1^{s_1} s^2 \bar{c}_s / \bar{c}_n \quad (1.6b)$$

$$\bar{c}_m = \sum_{s_2+1}^{s_3} \bar{c}_s \quad \bar{c}_n = \sum_1^{s_1} \bar{c}_s \quad (1.6c)$$

$$k_m^- = \sum_{s_2+1}^{s_3} k_s^- \bar{c}_s / \bar{c}_m \quad (1.6d)$$

$$R \equiv \sum_{s_1}^{s_2} (k_s^- \bar{c}_s)^{-1} \quad (1.6e)$$

where k_m^- is the mean dissociation rate constant of the micelles; \bar{c}_s is the concentration of one s -mer; \bar{c}_m is the total concentration of the micelles; \bar{c}_n is the total concentration of the oligomers; $\beta_m = \bar{c}_m / \bar{c}_1$; $\beta_n = \bar{c}_n / \bar{c}_1$; m and n are the mean aggregation numbers of the oligomers (including the free monomers) and of the micelles respectively; m_2 and n_2 are the second mathematical moments of the micellar and oligomer size distributions; σ_m and σ_n are the respective dispersions; R is the resistance of the transition region. (The equilibrium quantities are

denoted with a bar above the letter.) It has been established [14] that the one-step reaction mechanism, used by Lucassen, corresponds roughly to the slow process. In this case the above expressions simplify to: $\beta_n = 1$; $n = 1$; $\sigma_n = 0$; $n_2 = 1$; $\sigma_m = 0$; $m_2 = m^2$; $R = (k_m^- \bar{c}_m)^{-1}$. Equation (1.5) then reduces to

$$\tau_{\text{SL}} = [k_m^- (1 + m^2 \beta_m)]^{-1} \quad (1.7)$$

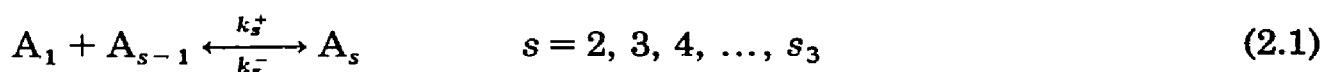
The theory of Lucassen [11] is successful in describing the main effect of the micelles on the dynamic surface elasticity of several surfactants when the slow relaxation process is of importance. But keeping in mind the more realistic model of Aniansson and Wall one may note that Lucassen's theory has two disadvantages: (i) it does not take into account the dispersion of the micelles σ_m which enters the expressions for τ_F and τ_{SL} (Eqns (1.4) and (1.5)), and (ii) it is not possible in the frame of Lucassen's theory to obtain a solution for E when the fast relaxation process is of importance.

Our aim in the present study is to develop a diffusion theory for the surface dilational modulus which accounts for the polydispersity of the micelles. Our theory allows a treatment of the mass transfer affected by either the fast process or the slow process of micellization.

First we will formulate the general equations, describing the micelles as polydisperse, diffusing and reacting particles and discuss the mathematical method of solution.

2. DIFFUSION EQUATIONS

We assume the reaction mechanism of formation of micelles to be



where A_s are the symbols of the s -mers; k_s^+ and k_s^- are the respective rate constants of association and dissociation of the s th reaction. The starting point of our mathematical consideration is the set of diffusion equations for the bulk concentrations of the species $c_s(x, t)$, corresponding to the reaction set shown in (2.1)

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - 2J_2 - \sum_3^{s_3} J_s \quad (2.2a)$$

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} + J_s - J_{s+1} \quad s = 2, 3, 4, \dots, s_3 \quad (2.2b)$$

$$J_s = k_s^+ c_1 c_{s-1} + k_s^- c_s \quad s = 2, 3, 4, \dots, s_3 \quad (2.3)$$

$$\sum_1^{s_3} sc_s = c \quad (2.4)$$

where D_s are the diffusivities of the s -mers; $J_s(x, t)$, given by Eqn (2.3), is the reaction (pseudo)flux, i.e. the total rate of the s th reaction. The local balance of the monomers (2.4) states that the total surfactant concentration $c(x, t)$ is not equal to the equilibrium value, \bar{c} , because there is diffusion and adsorption of surfactant material.

The solution of Eqns (2.2)–(2.4) has to obey the following boundary conditions for the components:

$$\frac{d}{dt}(A\Gamma) = AD_1 \left. \frac{\partial c_1}{\partial x} \right|_{x=0} \quad (2.5)$$

$$\Gamma = \bar{\Gamma} + (\partial\bar{\Gamma}/\partial\bar{c}_1)(c_1 - \bar{c}_1)|_{x=0} \quad (2.6)$$

$$\left. \frac{\partial c_s}{\partial x} \right|_{x=0} = 0 \quad s = 2, 3, 4, \dots, s_3 \quad (2.7)$$

$$c_s(\infty, t) = \bar{c}_s \quad s = 1, 2, 3, \dots, s_3 \quad (2.8)$$

Equation (2.5) represents the surface balance of monomers on a flat interface placed at $x=0$ (note, that the area, $A(t)$, varies with time). Equation (2.6) is an expansion of the adsorption, $\Gamma(t)$, in a series for small deviations from equilibrium while Eqn (2.7) means that aggregates with $s \geq 2$ do not adsorb. Finally, Eqn (2.8) states that the deviations from equilibrium vanish far from the solution surface.

In this type of experiment the diffusion time constant of the free monomers τ_D is given by the expression [16]

$$\tau_D = \frac{1}{D_1} \left(\frac{\partial\bar{\Gamma}}{\partial\bar{c}_1} \right)^2 \quad (2.9)$$

which is consistent also with the boundary conditions (2.5) and (2.6). The characteristic time of the experiment, ω^{-1} , can differ from τ_D . However, they must be of the same order of magnitude if we want to detect the effect of the exchange of material between the surface and the solution. Two important cases of diffusion exist, depending on the magnitude of the time constants ratio [16]. In general, the diffusion will be affected by the micellization kinetics only if τ_D is of the order of τ_F or τ_{SL} . If $\tau_D \approx \tau_F$ the fast relaxation process will be important for the behavior of the surface tension. In the other case ($\tau_D \approx \tau_{SL}$) the diffusion will be influenced by the slow relaxation process. Since at a given concentration τ_F is always much slower than τ_{SL} , the case $\tau_D \approx \tau_F \approx \tau_{SL}$ is most unlikely for the usual surfactants.

In our previous paper [16] a method for simplifying the complicated set of partial differential equations (2.2)–(2.4) is developed. As a result a set of only two equations is obtained. One of them is for the concentration of the free monomer, the other one is for the total concentration of the micelles. Below we shall consider separately the two cases of diffusion formulated above, i.e. $\tau_D \approx \tau_F$ and $\tau_D \approx \tau_{SL}$. We solve the respective diffusion equations for the monomers and the micelles to find expressions for the surface elasticity modulus.

3. DIFFUSION AFFECTED BY THE SLOW RELAXATION PROCESS

When $\tau_D \approx \tau_{SL}$, the diffusion of surfactant is affected by the slow relaxation process. In this case the diffusion equations in the bulk of solution reduce to [16]

$$\frac{\partial \xi_1}{\partial t} = D_1^* \frac{\partial^2 \xi_1}{\partial x^2} - \frac{m}{R\bar{c}_1(n_2\beta_n + \sigma_m^2\beta_m)} (m\xi_1 - \xi_m) \quad (3.1a)$$

$$\frac{\partial \xi_m}{\partial t} = D_m \frac{\partial^2 \xi_m}{\partial x^2} + \frac{1}{R\bar{c}_1\beta_m} (m\xi_1 - \xi_m) \quad (3.1b)$$

where ξ_1 and ξ_m are the relative deviations of the concentrations of the free monomers and of the micelles from equilibrium:

$$\xi_1(x, t) = (c_1 - \bar{c}_1)/\bar{c}_1 \quad \xi_m(x, t) = (c_m - \bar{c}_m)/\bar{c}_m \quad (3.2)$$

The constants in Eqns (3.1) are given by Eqns (1.6). Here we have introduced the effective diffusivity of the monomers D_1^* , which is represented as

$$D_1^* = \frac{D_n n_2 \beta_n + D_m \sigma_m^2 \beta_m}{n_2 \beta_n + \sigma_m^2 \beta_m} = d_1^* D_1 \quad (3.3)$$

D_1^* accounts for the effect of the micelles on the diffusivity of the free monomers. The mean diffusivities of the micelles D_m and the oligomers D_n are defined by

$$D_m = \sum_{s_2+1}^{s_3} D_s \bar{c}_s / \bar{c}_m = d_m D_1$$

and

$$D_n = \sum_1^{s_1} D_s \bar{c}_s / \bar{c}_n = d_n D_1$$

The source terms in the right-hand side of Eqns (3.1) give the net effect

of the micellization kinetics on the diffusion of the species. They are due to disintegration of the micelles during the slow relaxation process.

Combining Eqns (1.1), (2.5) and (2.6) and summing Eqns (2.7) and Eqns (2.8), we obtain the following boundary conditions for ξ_1 and ξ_m :

$$\frac{E}{E_G} = \left[1 - \frac{\delta_D}{\tau_D} \left(\frac{\partial \xi_1}{\partial x} \Big|_{x=0} \right) \left(\frac{\partial \xi_1}{\partial t} \Big|_{x=0} \right)^{-1} \right]^{-1} \quad (3.4a)$$

$$\xi_1(\infty, t) = 0 \quad (3.4b)$$

$$\frac{\partial \xi_m}{\partial x} \Big|_{x=0} = 0 \quad (3.4c)$$

$$\xi_m(\infty, t) = 0 \quad (3.4d)$$

where δ_D is the diffusion length and E_G is the Gibbs elasticity, defined as

$$\delta_D = \partial \bar{F} / \partial \bar{c}_1$$

and

$$E_G = -d\bar{\sigma}/d(\ln \bar{F})$$

Further, we shall determine the concentration of the free monomers ξ_1 , which in turn gives the elasticity modulus (cf. Eqn (3.4a)).

Following Lucassen [11] we assume that the solutions of the boundary-value problem formulated above can be represented as periodic functions of t

$$\xi_1(x, t) = \hat{\xi}_1(x) \exp(i\omega t) \quad \xi_m(x, t) = \hat{\xi}_m(x) \exp(i\omega t) \quad (3.5)$$

where $\hat{\xi}_1$ and $\hat{\xi}_m$ are functions of x . From (3.1), (3.4) and (3.5) we obtain the respective differential equations

$$\frac{d^2 \hat{\xi}_1}{dx^2} = a_1 \hat{\xi}_1 + a_m \hat{\xi}_m \quad (3.6a)$$

$$\frac{d^2 \hat{\xi}_m}{dx^2} = b_1 \hat{\xi}_1 + b_m \hat{\xi}_m \quad (3.6b)$$

and boundary conditions

$$\frac{E}{E_G} = \left[1 + \frac{i\delta_D}{\omega\tau_D} \frac{1}{\hat{\xi}_1(0)} \left(\frac{d\hat{\xi}_1}{dx} \Big|_{x=0} \right) \right]^{-1} \quad (3.7a)$$

$$\hat{\xi}_1(\infty) = 0 \quad (3.7b)$$

$$\frac{d\hat{\xi}_m}{dx} \Big|_{x=0} = 0 \quad (3.7c)$$

$$\hat{\xi}_m(\infty) = 0 \quad (3.7d)$$

The constants in (3.6) are

$$\begin{aligned} a_1 &= i\omega\tau_D/(d_1^* \delta_D^2) - ma_m & a_m &= -\alpha m\tau_{SL}/[(d_n n_2 \beta_n + d_m \sigma_m^2 \beta_m) R\bar{c}_1 \delta_D^2] \\ b_1 &= -\alpha m\tau_{SL}/[d_m \beta_m R\bar{c}_1 \delta_D^2] & b_m &= i\omega\tau_D/(d_m \delta_D^2) - b_1/m \end{aligned}$$

where $\alpha = \tau_D/\tau_{SL}$ is the Damköhler number, giving the ratio between the diffusion and the reaction terms in Eqns (3.1).

The boundary-value problem shown in Eqns (3.6)–(3.7) can be solved as shown in Ref. [11]. In this way we obtain the expression

$$\begin{aligned} \frac{E}{E_G} &= \left\{ 1 + (1-i)Z \left(\frac{1}{d_1^*} \right)^{1/2} (1-iX)^{1/2} \right. \\ &\quad \times \left\{ \left[1 + \left(\frac{d_m}{d_1^*} \right)^{1/2} (1-iX)^{1/2} \right]^2 - iX \frac{d_n - d_m}{d_1^*} \frac{n_2 \beta_n}{n_2 \beta_n + m_2 \beta_m} \right\}^{1/2} \\ &\quad \left. \times \left[1 - iK + \left(\frac{d_m}{d_1^*} \right)^{1/2} (1-iX)^{1/2} \right]^{-1} \right\}^{-1} \end{aligned} \quad (3.8)$$

for the complex elasticity modulus [17]. Here

$$\begin{aligned} Z &= (2\omega\tau_D)^{-1/2} & X &= (\omega\tau_{SL})^{-1} \\ K &= X(n_2 \beta_n + \sigma_m^2 \beta_m)/(n_2 \beta_n + m_2 \beta_m) \end{aligned}$$

The corresponding equation of Lucassen for monodisperse micelles (Eqn (3) in Ref. [11]) is a special case of our Eqn (3.8), when $K = k_m^-/\omega$ and $d_1^* = 1$ (for definitions of the other constants in this case see Section 1).

One can separate the real and the imaginary parts in Eqn (3.8). The results for the modulus $|E|$ and the phase ψ are

$$\frac{|E|}{E_G} = [1 + 2Z_m G_R + Z_m (G_R^2 + G_I^2)]^{-1/2} \quad (3.9)$$

$$\psi = \arctan \left(- \frac{Z_m G_R}{1 + Z_m G_I} \right) \quad (3.10)$$

where we have introduced the notations

$$Z_m = Z(|F||B|/d_1^*)^{1/2}/(C_R^2 + C_I^2)$$

$$F = 1 - iX \quad |F| = (1 + X^2)^{1/2}$$

$$|B| = (B_R^2 + B_I^2)^{1/2} \quad B_R = 1 + d_m/d_1^* + 2F_m \cos \phi$$

$$B_I = -(Xd_m/d_1^*) + X(d_m - d_n)n_2\beta_n/[d_1^*(n_2\beta_n + m_2\beta_m)] + 2F_m \sin \phi$$

$$F_m = (|F|d_m/d_1^*)^{1/2} \quad \phi = [\arctan(-X)]/2$$

$$C_R = 1 + F_m \cos \phi \quad C_I = -K + F_m \sin \phi$$

$$G_R = (C_R - C_I) \cos \gamma + (C_R + C_I) \sin \gamma$$

$$G_I = -(C_R + C_I) \cos \gamma + (C_R - C_I) \sin \gamma$$

$$\gamma = \phi + [\arctan(B_I/B_R)]/2$$

(the subscripts R and I denote real and imaginary parts respectively).

If the solution does not contain micelles ($\beta_m = 0$, $\beta_n = 1$, $n_2 = 1$, $d_1^* = 1$, $X = K$) the Eqns (3.8)–(3.10) transform into the corresponding equations of Lucassen and van den Tempel [2]

$$\frac{E}{E_G} = \frac{1 + Z + iZ}{1 + 2Z + 2Z^2} \quad (3.11a)$$

$$\frac{|E|}{E_G} = \frac{1}{(1 + 2Z + 2Z^2)^{1/2}} \quad (3.11b)$$

$$\psi = \arctan\left(\frac{Z}{1 + Z}\right) \quad (3.11c)$$

4. DIFFUSION AFFECTED BY THE FAST RELAXATION PROCESS

If the fast relaxation process affects the mass transfer ($\tau_D \approx \tau_F$), the bulk diffusion can be described by the equations

$$\frac{\partial \xi_1}{\partial t} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - k_m^- \beta_m \left(\xi_1 - \frac{1}{\sigma_m^2} \Xi_m \right) \quad (4.1a)$$

$$\frac{\partial \Xi_m}{\partial t} = D_m \frac{\partial^2 \Xi_m}{\partial x^2} + k_m^- \left(\xi_1 - \frac{1}{\sigma_m^2} \Xi_m \right) \quad (4.1b)$$

derived in Ref. [16]. Equation (4.1a) accounts for the diffusion of the free monomers, while Eqn (4.1b) refers to the monomers which are aggregated in micelles. Ξ_m is the relative deviation from equilibrium

of the concentration of the aggregated monomers, defined as

$$\Xi_m(x, t) = \sum_{s_2+1}^{s_3} s \bar{c}_s \xi_s / \bar{c}_m \quad (4.2)$$

Ξ_m is used instead of ξ_m , because the total concentration of the micelles remains approximately constant, when the diffusion is influenced by the fast relaxation process, i.e. $\xi_m = 0$ (see Ref. [16]). However, the micelles of different aggregation number s can diffuse, forced by the respective concentration gradients.

To solve Eqns (4.1) we use Eqns (3.4a) and (3.4b) as boundary conditions for the function ξ_1 . The boundary conditions for the function Ξ_m are

$$\left. \frac{\partial \Xi_m}{\partial x} \right|_{x=0} = 0 \quad (4.3a)$$

$$\Xi_m(\infty, t) = 0 \quad (4.3b)$$

To derive Eqns (4.3), Eqns (2.7) and (2.8) are first multiplied by s and then summed over the micellar region. We search again for a periodic solution of the problem (cf. (3.5))

$$\xi_1(x, t) = \hat{\xi}_1(x) \exp(i\omega t) \quad \Xi_m(x, t) = \hat{\Xi}_m(x) \exp(i\omega t) \quad (4.4)$$

Equations (4.1) and (4.4) give

$$\frac{d^2 \hat{\xi}_1}{dx^2} = a_1 \hat{\xi}_1 + a_m \hat{\Xi}_m \quad (4.5a)$$

$$\frac{d^2 \hat{\Xi}_m}{dx^2} = b_1 \hat{\xi}_1 + b_m \hat{\Xi}_m \quad (4.5b)$$

where new constants are introduced

$$\begin{aligned} a_1 &= i\omega\tau_D/\delta_D^2 - \sigma_m^2 a_m & a_m &= -\alpha\tau_F k_m^- \beta_m / (\sigma_m^2 \delta_D^2) \\ b_1 &= -\alpha\tau_F k_m^- / (d_m \delta_D^2) & b_m &= i\omega\tau_D / (d_m \delta_D^2) - b_1 / \sigma_m^2 \end{aligned}$$

where $\alpha = \tau_D/\tau_F$ is in fact the Damköhler number for the fast process. Solving the problem as in the preceding section we obtain the complex elasticity modulus

$$\begin{aligned} \frac{E}{E_G} &= \left\{ 1 + (1-i)Z(1-iX)^{1/2} \left\{ [1 + d_m^{1/2}(1-iX)^{1/2}]^2 - iK(1-d_m) \right\}^{1/2} \right. \\ &\quad \left. \times [1 - iK + d_m^{1/2}(1-iX)^{1/2}]^{-1} \right\}^{-1} \quad (4.6) \end{aligned}$$

where

$$X = (\omega\tau_F)^{-1} \quad K = X/(1 + \sigma_m^2\beta_m)$$

The separation of the real and imaginary parts of Eqn (4.6) leads to the same equations for the elasticity modulus $|E|$ and the phase ψ as Eqns (3.9) and (3.10). The definitions of the constants remain the same except that now:

$$B_R = 1 + d_m + 2(d_m|F|)^{1/2} \cos \phi$$

$$B_i = -d_m X + K(1 - d_m) + 2(d_m|F|)^{1/2} \sin \phi$$

$$C_R = 1 + (d_m|F|)^{1/2} \cos \phi$$

$$C_i = -K + (d_m|F|)^{1/2} \sin \phi$$

When micelles are absent ($K = X$) the corresponding equations (3.11) are a special case of our equations for E , $|E|$ and ψ .

Equation (4.6) cannot be obtained in the frame of Lucassen's model because the fast process is a result of the polydispersity of micelles.

5. DISCUSSION

We discuss first the case where the diffusion is affected by the slow relaxation process. The effect of the polydispersity of the micelles on the elasticity modulus $|E|$ and the phase ψ is shown in Figs 1 and 2 respectively. The curves are drawn by means of Eqns (3.9) and (3.10). The values of the constants are chosen in such a way that our results and the results of Lucassen for monodisperse micelles [11] are comparable.

Let us consider first the behavior of the system when there are no micelles in the solution. The mechanical energy of the periodical oscillations transforms into elastic energy of the adsorption layer. In the experiment of Lucassen low molecular weight surfactants which are soluble in the water phase were used. That is why the dissipation of the energy in the adsorption layer is due to the exchange of molecules between the surface and the solution rather than to the interactions (friction) between the adsorbed surfactant molecules. The easier the molecules pass from the adsorption layer in the solution and vice versa, the greater will be E_i and ψ (see Eqn (1.3) and Fig. 2) and, hence, the greater will be the effective surface viscosity. If the oscillations are too fast ($\omega^{-1} \ll \tau_D$), the diffusion of surfactant does not influence the adsorption layer. The layer behaves as though the surfactant is not soluble. In this case $Z \ll 1$ and Eqn (3.11b) gives $|E_G| \rightarrow E_G$ (Fig. 1) while it follows from Eqn (3.11c) that $\psi \rightarrow 0$ (Fig. 2). There is no dissipation

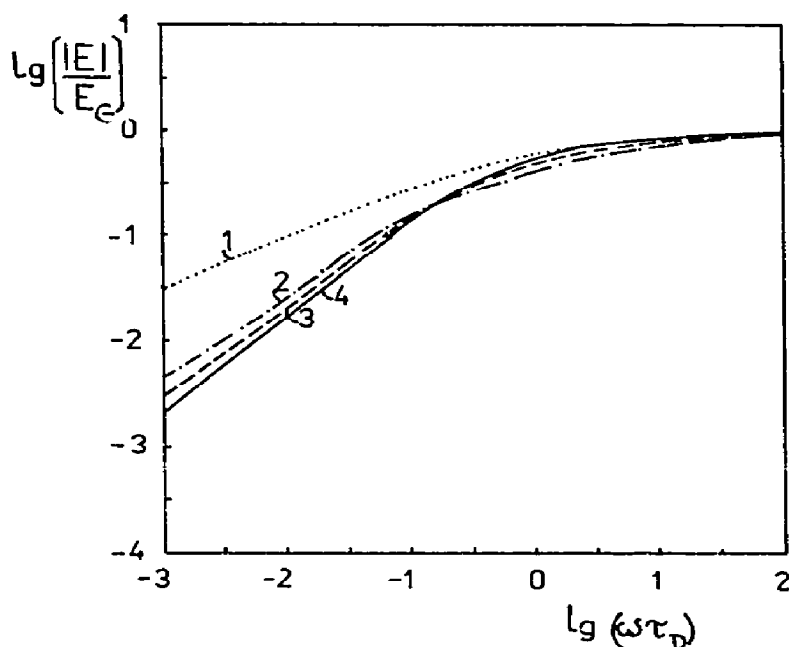


Fig. 1. Dependence of the surface elasticity modulus $|E|$ on ω , when the diffusion is affected by the slow relaxation process of micellization. Curve 1 corresponds to the case when micelles are absent from the solution, Eqn (3.11b). The other curves are drawn from Eqn (3.9) for micellar solutions, containing micelles with different dispersions σ_m ; curve 2, $\sigma_m = 20$; curve 3, $\sigma_m = 10$; curve 4, $\sigma_m = 0$ (model of Lucassen). The remaining constants are: $d_m = 0.25$; $d_n = 1$; $n_2 = 1$; $n = 1$; $m = 50$; $\beta_n = 1$; $\beta_m = 0.02$; $R = 2 \cdot 10^{11} \text{ cm}^3 \text{ s mol}^{-1}$; $\bar{c}_1 = 2.5 \cdot 10^8 \text{ cm}^3 \text{ mol}^{-1}$.

of energy ($E_I \rightarrow 0$), because the surfactant molecules do not cross into and from the solution. In the other limit (extremely slow oscillations, $\omega^{-1} \gg \tau_D$) the adsorption layer loses its elastic properties, because the transfer of molecules is too fast: $|E| \ll E_G$ (Fig. 1) and $E_I = E_R$ ($\psi = 45^\circ$) (Fig. 2). Most pronounced are these alterations when $\omega^{-1} \approx \tau_D$ ($Z \approx 2^{-1/2} \approx 0.71$, $|E| \approx 0.54E_G$ and $\psi \approx \pi/8$).

Let us consider now the effect of the micelles on the behavior of the adsorption layer. At a given frequency of oscillations the modulus $|E|$ is smaller than in the case without micelles (Fig. 1). The micelles enhance the exchange of monomers with the adsorption layer, because they can diffuse and disintegrate simultaneously. This leads to a notable maximum in E_I/E_R or, what is the same, in the phase ψ (Fig. 2). Under the otherwise equal conditions the micelles with zero dispersion produce the biggest surface viscosity (model of Lucassen). When the micelles are polydisperse, as in our model, the height of the maximum decreases. This may be explained by the fact that the monodisperse micelles disrupt at once releasing many more monomers than poly-

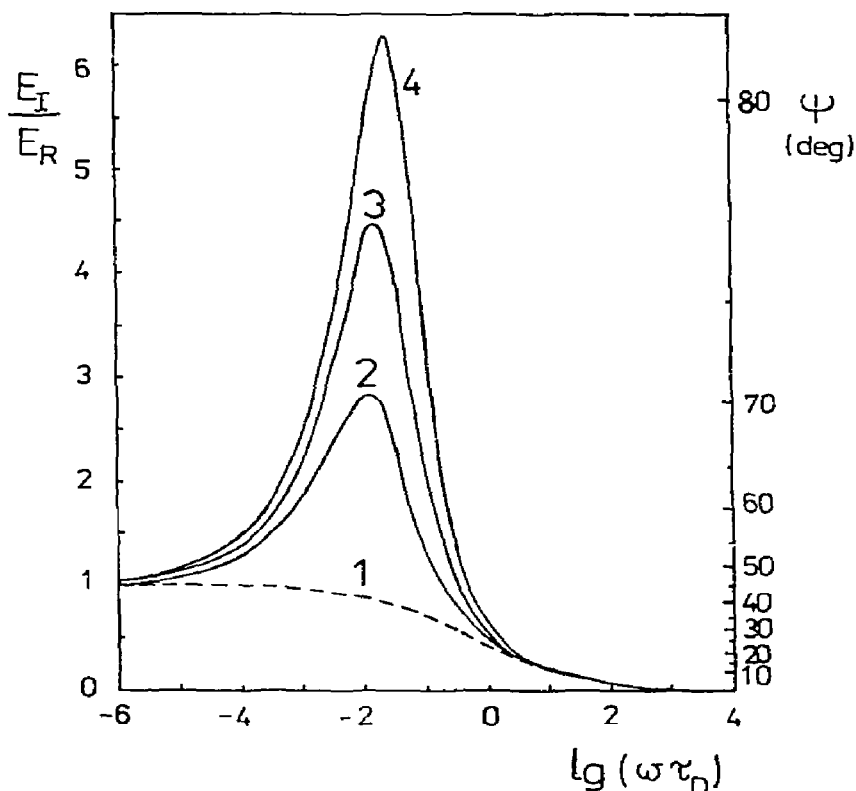


Fig. 2. Dependence of the phase $\psi = \arctan(E_I/E_R)$ on ω at different values of the dispersion of the micelles σ_m . Curve 1 is for solution without micelles, Eqn (3.11c). Curves 2, 3 and 4 are plotted from Eqn (3.10) for micelles with $\sigma_m = 20$, curve 2; $\sigma_m = 10$, curve 3; $\sigma_m = 0$, curve 4 (model of Lucassen). The other parameters are as in Fig. 1.

disperse micelles having the same bulk concentration, \bar{c}_m , but disintegrating by the many-steps mechanism (2.1).

From the experimental data of Lucassen we computed the parameters of the micellar distribution in solutions of hexadecyl dimethylammonio-propane sulfonate (HDPS). We used the data of $|E|$ measured for five different concentrations of HDPS (above the CMC) at five frequencies (see Fig. 3). The numerical procedure used by us consists of the following steps: (i) At each point we subtract the experimental value of $|E|$ from the value calculated by Eqn (3.9). (ii) We take the sum of the squares of these differences for all points. (iii) We minimize this sum numerically by varying the parameters m , σ_m and τ_{SL} . (Note, that the mean aggregation number m and the dispersion σ_m do not depend on the concentration.) The minimization method of Hooke and Jeeves (quoted in Ref. [18]) is used. (iv) Finally we compute the theoretical curves for $E_I/E_R = \tan \psi$ (Fig. 4) using the constants obtained from the data of $|E|/E_G$ in Fig. 3.

The diffusion time of HDPS is $\tau_D = 0.725$ s; it remains constant above

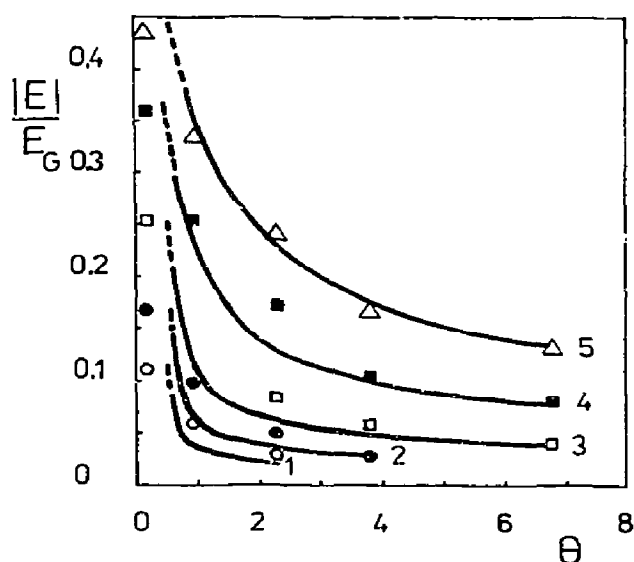


Fig. 3. Data of Lucassen [11] for the surface elasticity modulus $|E|$ of micellar solutions of HDPS (28°C), plotted vs the relative concentration of the aggregated monomers θ . The values of ω are 0.052 s^{-1} (\circ), curve 1; 0.105 s^{-1} (\bullet), curve 2; 0.209 s^{-1} (\square), curve 3; 0.524 s^{-1} (\blacksquare), curve 4; 1.047 s^{-1} (\triangle), curve 5. The (solid) curves are drawn from Eqn (3.9) at $\bar{c}_1 = 2.55 \cdot 10^{-8} \text{ mol cm}^{-3}$; $\tau_D = 0.725 \text{ s}^{-1}$ and $d_m = 0.25$ [11]; $d_n = 1$; $n_2 = 1$; $n = 1$; $\beta_n = 1$; $m = 45$; $\sigma_m = 15$. The values used for τ_{SL} are given by Eqn (5.1) (see Fig. 5).

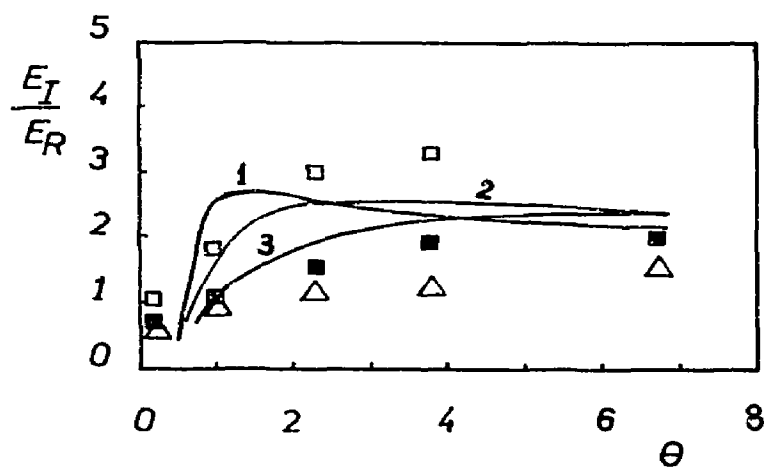


Fig. 4. Data of Lucassen [11] for the ratio E_I/E_R (i.e. the phase ψ) of micellar solutions of HDPS (28°C) vs θ at different ω : 0.209 s^{-1} (\square), curve 1; 0.524 s^{-1} (\blacksquare), curve 2; 1.047 s^{-1} (\triangle), curve 3. The (solid) curves are drawn from Eqn (3.10) using the values for m , σ_m and τ_{SL} , computed from the data of elasticity modulus in Fig. 3.

the CMC because the concentration of the free monomer does not change ($\bar{c}_1 = 2.55 \cdot 10^{-8} \text{ mol cm}^{-3}$). The ratio d_m is accepted to be $d_m = 0.25$ (Lucassen). We assume for the oligomers that $d_n = 1$, $n_2 = 1$ and $\beta_n = 1$. The micellar constants of HDPS, calculated by our theory,

are $m = 45$ and $\sigma_m = 15$. Note that these are the first constants of the polydisperse micellar distribution to be determined by means of a surface experiment.

The computed slow relaxation time $\tau_{SL}(\theta)$ is given in Fig. 5 as a function of the relative concentration θ

$$\theta = (\bar{c} - \bar{c}_1)/\bar{c}_1 = m\bar{c}_m/\bar{c}_1 = m\beta_m$$

To compute the solid lines in Figs 3 and 4 we used the numerical fit of τ_{SL}

$$\tau_{SL}^{-1} = -1.49425 + 2.65949\theta \quad (5.1)$$

At the lowest concentrations the linear fit of Eqn (5.1) fails. That is why the solid curves in this region cannot be drawn theoretically (dashed lines in Fig. 3).

The dashed line in Fig. 5 corresponds to Eqn (1.7) (model of Lucassen). The constants used are as determined by Lucassen [11]: $m = 50$ and $k_m^- = 0.154 \text{ s}^{-1}$. It may be expected that the time constants τ_{SL} calculated by the model of Lucassen will be somewhat lower than those predicted by the polydisperse theory of the micellization kinetics. The main advantage of our theory is that it also allows the computation of the

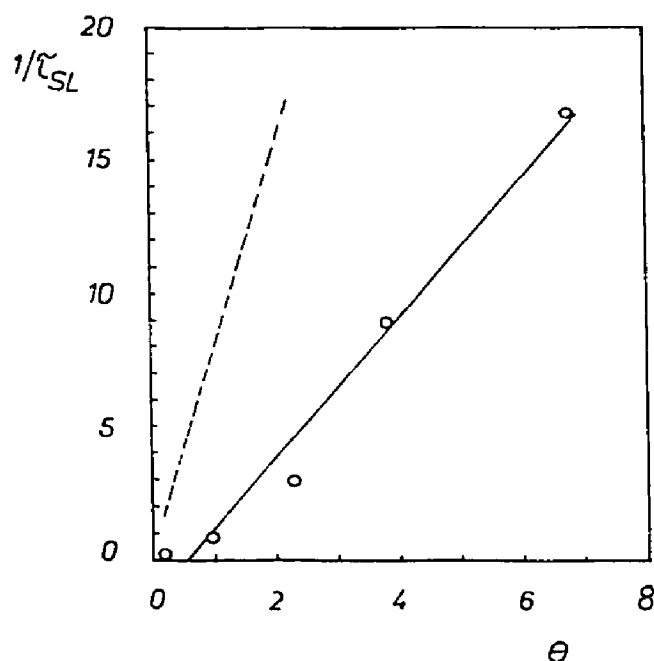


Fig. 5. Concentration dependence of the reverse slow relaxation time $1/\tau_{SL}$ of HDPS. The values of τ_{SL} (circles) are computed from the data of Lucassen [11] by our polydisperse model at $\sigma_m = 15$ and $m = 45$ (see the text). The solid line corresponds to Eqn (5.1). The dashed line is drawn from Eqn (1.7) for monodisperse micelles, having $\sigma_m = 0$, $m = 50$, $k_m^- = 0.154 \text{ s}^{-1}$.

dispersion of the micelles, σ_m . Unfortunately, experimental data for HDPS from bulk experiments are not available in the literature. The values of the micellar constants of HDPS, received by us, are of the same order as the constants of many typical surfactants, published in Refs [15 and 19].

We shall consider now the case when the diffusion is affected by the fast relaxation process. In Fig. 6 we have shown E_I/E_R as a function of the frequency at different θ . The numerical values of the constants are for SDS (sodium dodecyl sulfate): $\tau_D = 1.2 \cdot 10^{-6}$ s; $d_m = 0.18$ ($D_1 = 5.8 \cdot 10^{-6}$ cm² s⁻¹ and $D_m = 10^{-6}$ cm² s⁻¹ [20]); $k_m = 10^7$ s⁻¹, $m = 64$ and $\sigma_m = 13$ [15]. It is seen that the phase ψ increases when the micelle concentration (i.e. θ) increases. In this way the viscous behavior of the adsorption layer becomes appreciable because the micelles enhance the supply of monomers in the adsorption layer. The characteristic diffusion time of SDS is much smaller than that of HDPS which is why one needs much higher frequencies of oscillation (of the order of 10^4 – 10^5 Hz) in order to satisfy the condition $\omega^{-1} \approx \tau_D$. Such high frequencies are not accessible in the mechanical methods [2–5]. They can be realized by light scattering from the surface thermal fluctuations [6,7].

Finally we shall discuss the case of micellization kinetics, described as a pseudo-first order reaction. The complicated reaction of formation of micelles can be represented roughly as a pseudo-first order reaction

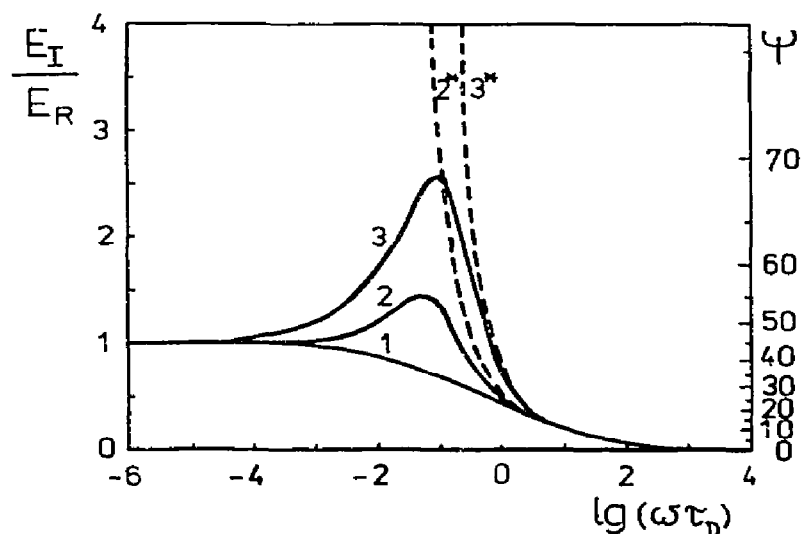


Fig. 6. Dependence of E_I/E_R and the phase ψ on ω , when the fast relaxation process affects the diffusion. The constants used are for SDS (see the text). The solid curves correspond to different concentrations of the aggregated monomers θ : $\theta = 0$, $\alpha = 0$ (without micelles), curve 1 (Eqn (3.11c)); $\theta = 1$, $\alpha = 0.26$, curve 2 (Eqn (4.6)); $\theta = 5$, $\alpha = 1$, curve 3. The dashed lines 2* and 3* represent the approximate solution of Eqn (5.7).

with characteristic time τ_M , equal to either τ_F or τ_{SL} . The reverse time $1/\tau_M$ is not yet a rate constant of an elementary first-order reaction, but it is a complex function of the rate constants of the reaction mechanism (2.1) and of the concentration too. In this case the micellar system appears as a quasi-closed system, where the total surfactant concentration does not change locally, i.e.

$$c(x, t) \approx \bar{c} \quad (5.2)$$

However, the concentrations of the individual species (*s*-mers) can vary with time (for more details see Ref. [16]). Two additional relations between the functions in the diffusion equations are established in this case [16]:

$$(n_2\beta_m + \sigma_m^2\beta_m)\hat{\xi} + m\beta_m\hat{\xi}_m = 0 \quad (5.3a)$$

(diffusion affected by the slow relaxation process) and

$$\hat{\xi}_1 + \beta_m\hat{\xi}_m = 0 \quad (5.3b)$$

(diffusion affected by the fast process). However, it is shown in Ref. [16] that the assumption (5.2) is equivalent to the following relationship for the diffusivities:

$$D_m \approx D_n \approx D_1^* \approx D_1 \quad (5.4)$$

In reality the diffusivity of the micelles is several times lower than the diffusivity of the free monomers. For example, for HDPS $d_m = 0.25$ and for SDS $d_m = 0.18$ (see above). Nevertheless, the hypothesis (5.2) (or, what is the same, (5.4)) may be important for some practical cases where the analytical solution of (3.1) and (4.1) is impossible (e.g. the kinetics of the surface tension [16]).

In both cases considered in Sections 3 and 4, the set of two diffusion equations reduces to one equation

$$\frac{\partial \hat{\xi}_1}{\partial t} = D_1 \frac{\partial^2 \hat{\xi}_1}{\partial x^2} - \frac{1}{\tau_M} \hat{\xi}_1 \quad (5.5)$$

Equation (5.5) is a generalization of the pseudo-first order reaction model for diffusion problems. The equation for the function $\hat{\xi}_1(x)$

$$\frac{d^2 \hat{\xi}_1}{dx^2} - \frac{1}{\delta_D^2} (i\omega\tau_D + \alpha) \hat{\xi}_1 = 0 \quad (5.6)$$

follows from Eqn (5.4). Solving (5.6) we obtain

$$\frac{E}{E_G} = [1 + (1 - i)Z(1 - iX)^{1/2}]^{-1} \quad (5.7)$$

Equation (5.7) can be obtained also if we set, in Eqns (3.8) and (4.6), $d_m = d_n = 1$ (cf. Eqn (5.4)).

The dashed lines in Fig. 6 are plotted from Eqn (5.7). The area of validity of the assumptions (5.2) or (5.4) can be seen. This approximation can be used at sufficiently high frequencies when $\omega \gg k_m^- / \sigma_m^2$ (of the order of $5.9 \cdot 10^4 \text{ s}^{-1}$ for SDS). Under these conditions the micelles appear effectively as immobile surfactant sources with respect to the monomers, because the micelles diffuse as fast as the free monomers do.

CONCLUSION

A theory of the effect of polydisperse micelles on the surface elasticity modulus of surfactant solutions subjected to periodic oscillations with small amplitude is developed. The adsorption kinetics are assumed to be diffusion controlled. The micellization kinetics could affect the surface elasticity if the time constant of the fast relaxation process τ_F or that of the slow process τ_{SL} is comparable with the characteristic diffusion time τ_D . Two important cases of surfactant diffusion are considered: $\tau_{SL} \approx \tau_D$ and $\tau_F \approx \tau_D$.

If the diffusion is affected by the slow relaxation process, expressions for the complex elasticity modulus E , for $|E|$ and for the phase ψ are derived. These equations give, as special cases, the equation for E of Lucassen [11] for monodisperse micelles and the corresponding equations of Lucassen and van den Tempel [2] for solutions without micelles. The parameters of the micelle size distribution of HDPS (mean aggregation number m and dispersion σ_m) are computed from the experimental data of Lucassen [11]. The calculated values $m = 45$ and $\sigma_m = 15$ agree with the values of the parameters for other surfactants, obtained by chemical relaxation techniques [15,19].

When the diffusion is affected by the fast relaxation process, equations for E , $|E|$ and ψ are derived. These equations cannot be obtained in the frame of Lucassen's model, because the fast relaxation process is a result of the polydispersity of the micelles.

In both cases the micelles enhance the exchange of monomers between the adsorption layer and the solution, thus making the effective viscous behavior of the adsorption layer more pronounced. The main advantage of the proposed theory is that the treatment of surfactant diffusion, affected not only by the slow relaxation process of micellization but also by the fast relaxation process, is possible. The time constants of micellization τ_F and τ_{SL} computed by our theory from surface experiments are consistent with those computed from bulk experiments by the theory of Aniansson and co-workers [13–15].

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APPENDIX: LIST OF SYMBOLS

A	Surface area
A_s	Chemical symbol of one s -mer
c	Total surfactant concentration
c_s	s -mer concentration
c_m, c_n	Total micelle and oligomer concentrations
d_1	Dimensionless monomer diffusivity
d_m, d_n	Dimensionless mean micelle and oligomer diffusivities
D_s	s -mer diffusivity
D_m, D_n	Mean micelle and oligomer diffusivities
E	Surface elasticity modulus

E_G	Gibbs' elasticity modulus
J_s	Total rate of the sth reaction
i	$\sqrt{-1}$
k_m^-	Mean micelle rate constant
k_s^+, k_s^-	Association and dissociation rate constants of the sth reaction
m, n	Mean aggregation numbers of micelles and oligomers
m_2, n_2	Second moments of micelle and oligomer size distribution
R	Resistance of the transition region
s	Aggregation number
t	Time
x	Space variable

Greek letters

α	Damköhler number
β_s	Dimensionless s -mer concentration
β_m, β_n	Dimensionless micelle and oligomer concentrations
Γ	Adsorption
δ_D	Diffusion length
θ	Excess surfactant concentration aggregated in micelles
ξ_s	Relative deviation of s -mer concentration from equilibrium
ξ_m	Relative deviation of total micelle concentration
$\bar{\xi}_m$	Relative deviation of the concentration of monomers aggregated in micelles
σ	Surface tension
σ_m, σ_n	Dispersions of micelle and oligomer size distribution
τ_D	Diffusion time constant
τ_F	Fast relaxation time
τ_{SL}	Slow relaxation time
ψ	Oscillation retarding phase
ω	Angular velocity