

INTERFACIAL RHEOLOGY AND KINETICS OF ADSORPTION FROM SURFACTANT SOLUTIONS

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ABSTRACT

A theoretical approach to the diffusion controlled kinetics of adsorption on the expanding interface of surfactant solutions is developed and compared with the experiment. This approach being an analogue of von Karman's approach to the hydrodynamic boundary layer is applicable to both submicellar and micellar surfactant solutions under large deviations from equilibrium. The partial differential equations of the convective diffusion are reduced to a set of ordinary differential equations of first order and algebraic equations. This simplifies the numerical computations and enhances the interpretation of the experimental data. Dynamic surface tension data for solutions of sodium dodecyl sulfate obtained by the maximum bubble pressure method are interpreted. Reasonable results for the diffusivity of monomers and the rate constant of micellar disintegration have been obtained.

A local approach to interfacial rheology is briefly considered. The applicability of this approach to studies of visco-elastic dilational properties of adsorption layers from low molecular surfactants and proteins is demonstrated.

1. INTRODUCTION

The kinetic adsorption properties of surfactants are a factor of crucial importance for the stability of emulsions and foams. The interface is subjected to large deformations and is far from equilibrium in the practical processes of dispersions preparation. The same is true for dynamic experimental methods like the maximum bubble pressure and drop volume methods which are often used for

studies of the adsorption kinetics from surfactant solutions. This complicates the interpretation of the experimental results obtained by these methods. Particularly, the mathematical boundary problem can not be linearized and partial differential equations of convective diffusion have to be solved numerically along with nonlinear boundary conditions. The situation is even more complicated if aggregates of surfactant molecules (micelles) are present in the solution. We have proposed a method which reduces the problem to a set of ordinary differential equation(s) and algebraic equations^{1,2}. This simplifies the computations and enhances the interpretation of the experimental data. A brief outline of the theory and interpretation of dynamic surface tension data obtained by the maximum bubble pressure method in submicellar and micellar surfactant solutions are given in the second section of the present work.

The interfacial adsorption layers of surfactant become more dense and approach their equilibrium state at sufficiently long times of adsorption. The resistance of the adsorption layers against small deformations caused by the collisions between the fluid particles in dispersions is one of the main factors governing the long time stability of the droplets in emulsions or the bubbles in froth flotation. In terms of the interfacial rheology³ the deformation of an interface gives rise to stresses stemming from the interfacial tension σ and two others proportional to the interfacial dilational and shear viscosities, η_d and η_{sh} . It is usually assumed that the interfacial viscous stresses are proportional to the rate of *total* (macroscopic) deformation^{3,4}. Based on the idea that the energy dissipation in the interfacial layer is determined by the mutual displacement of the surfactant molecules we have proposed an alternative approach⁵. We have formulated a new rheological equation relating the surface viscous stress to the local (rather than to the total) rate of dilation. The results are applied to interpret the data from an experimental method developed by us for studying the dilatational visco-elastic properties of the adsorption layers^{5,6}. The results obtained with low molecular surfactants and proteins are summarised in section 3.

2. KINETICS OF ADSORPTION FROM SURFACTANT SOLUTIONS UNDER DIFFUSION CONTROL

The theoretical treatment of this problem consists in solving the respective diffusion equation(s) under appropriate boundary conditions. In general, this is a nonlinear boundary problem. One source of nonlinearity is the relation between the subsurface concentration of surfactant monomers, c_{10} , and the surfactant adsorption, Γ . In the case of diffusion controlled adsorption it is usually assumed that the instantaneous values of c_{10} and Γ are connected by the equilibrium adsorption isotherm:

$$c_{10} = c_{10}(\Gamma) \quad [2.1]$$

For instance, it can be the Langmuir adsorption isotherm, which is operative for nonionic⁷ and ionic⁸ surfactants. Recently we proposed a considerably simpler and less time consuming method for solving the nonlinear boundary problem¹. This method, which is analogous to the von Karman approach to the hydrodynamic boundary layer (see e.g. Ref. (9)), was successfully applied for interpretation of data provided by the maximum bubble pressure technique for surfactant solutions below the critical micellization concentration (CMC)¹⁰. Further, we extended our approach to surfactant concentrations above CMC².

Since the micelles are unstable species, they can enhance essentially the transport of monomers from the bulk to the interface or backwards. Both surfactant monomers and micelles are involved in the diffusion transport toward the surface accompanied with mass exchange between these two species (i.e. chemical reaction). This complicates additionally the nonlinear boundary problem. In the case of an isotropic surface dilation the surface mass balance equation reads

$$\frac{d\Gamma}{dt} + \dot{\alpha}(t)\Gamma(t) = D_1 \left. \frac{\partial c_1}{\partial x} \right|_{x=0} \quad [2.2]$$

where D_1 is the monomer diffusivity, $c_1(x,t)$ is the monomer concentration; the plane $x = 0$ corresponds to the solution surface, and the x -axis is directed inwards to the solution. $\dot{\alpha}$ is the rate of surface dilation defined as

$$\dot{\alpha} = \frac{1}{A} \frac{dA}{dt}, \quad [2.3]$$

where A is the area. Since, in general, the interfacial dilation is coupled with some convective flow in the bulk of solution, the bulk monomer concentration obeys the equation of convective diffusion¹⁶

$$\frac{\partial c_1}{\partial x} - \dot{\alpha} x \frac{\partial c_1}{\partial x} = D_1 \frac{\partial^2 c_1}{\partial x^2} + m k_d c_m - m k_a c_1^m \quad [2.4]$$

The last two terms in Eq. [2.4] express the source and drain of monomers due to presence of micelles. In particular, c_m is the concentration of the micelles, m is their aggregation number, k_a and k_d are the rate constants of the micellar assembly and disassembly:



(here A_m and A_1 symbolise micelle and monomer). This reaction scheme is a limiting case of a stepwise reaction mechanism of micellization¹⁸.

Analogously, one can write the diffusion equation for the micelles:

$$\frac{\partial c_m}{\partial t} - \dot{\alpha} x \frac{\partial c_m}{\partial x} = D_m \frac{\partial^2 c_m}{\partial x^2} + k_a c_1^m - k_d c_m \quad [2.6]$$

Here D_m is the diffusion coefficient of the micelles.

The boundary conditions are

$$c_1(0, t) = c_{10}(t), \quad \lim_{x \rightarrow \infty} c_1(x, t) = c_{1\infty} = \text{const} \quad [2.7]$$

$$c_m(0, t) = c_{m0}(t), \quad \lim_{x \rightarrow \infty} c_m(x, t) = c_{m\infty} = \text{const} \quad [2.8]$$

$$\lim_{x \rightarrow \infty} \frac{\partial c_1}{\partial x} = \lim_{x \rightarrow \infty} \frac{\partial c_m}{\partial x} = 0 \quad [2.9]$$

c_{m0} in Eq. [2.8] denotes the subsurface concentration of the micelles, while $c_{1\infty}$ and $c_{m\infty}$ stand for the bulk concentrations of surfactant monomers and micelles far from the surface. Since the micelles do not adsorb, the micellar flux at the interface must be zero, i.e.

$$\frac{\partial c_m}{\partial x} = 0 \quad \text{at } x = 0 \quad [2.10]$$

One can introduce the quantities

$$l_1(t) = \frac{1}{c_{1\infty}} \int_0^{\infty} [c_{1\infty} - c_1(x,t)] dx \quad [2.11]$$

$$l_m(t) = \frac{1}{c_{m\infty}} \int_0^{\infty} [c_{m\infty} - c_m(x,t)] dx. \quad [2.12]$$

l_1 represents the thickness of an imaginary layer adjacent to the interface, which contains an amount of free monomers (of uniform concentration $c_{1\infty}$) equal to the deficiency of monomers in a vicinity of the real interface caused by the surfactant adsorption. l_m has analogous meaning concerning the micelles. After integration of Eqs. [2.4] and [2.6] from $x = 0$ to $x = \infty$ an expression for $(\partial c_1 / \partial x)_{x=0}$ can be derived, which upon substitution in Eq. [2.2] and subsequent integration from $t=0$ to t under assumption $l_1(0) = l_m(0) = 0$ yields

$$\Gamma(t) = \frac{A_0}{A(t)} \Gamma_0 + c_{1\infty} l_1(t) + m c_{m\infty} l_m(t), \quad [2.13]$$

where $A_0=A(0)$ and $\Gamma_0=\Gamma(0)$. Eq. [2.13] implies that the instantaneous adsorption, $\Gamma(t)$, depends on two *integrals*, $l_1(t)$ and $l_m(t)$, of the concentration profiles $c_1(x,t)$ and $c_m(x,t)$. Since the integrals are not too sensitive to the local behaviour of the concentration profiles to obtain the time dependence of the interfacial properties (adsorption, surface tension, etc.) one can use model profiles for $c_1(x)$ and $c_m(x)$ instead of the exact solutions of the respective diffusion equations. In order to provide adequacy between the model profiles, $c_1^*(x,t)$ and $c_m^*(x,t)$ (see Fig. 1), and the real concentration profiles, the following conditions have been imposed²: (i) equivalence between integral quantities $l_1(t)$ and $l_m(t)$ calculated from the model and real profiles; (ii) $\partial c_1^* / \partial x = \partial c_1 / \partial x$ and $\partial^2 c_m^* / \partial x^2 = \partial^2 c_m / \partial x^2$ at $x = 0$; (iii) the model profiles should not exhibit any singularities at any x i.e. $\partial c_1 / \partial x$ and $\partial c_m / \partial x$ should be continuous functions of the distance x . After simple mathematical computations the following final set of equations has been obtained²

$$c_{1\infty} l_1(t) = \frac{\pi - 2}{\pi} [c_{1\infty} - c_{10}(t)] \delta_1(t) \quad [2.14]$$

$$c_{m\infty} l_m(t) = \frac{1}{2} [c_{m\infty} - c_{m0}(t)] \delta_m(t) \quad [2.15]$$

$$\frac{d c_{m0}}{d t} = \frac{\pi^2 D_m}{2 \delta_m^2} [c_{m\infty} - c_{m0}(t)] - k_d c_{m0}(t) + k_a c_{10}^m(t) \quad [2.16]$$

$$\frac{d l_1}{d t} + \dot{\alpha} l_1 = \frac{(\pi-2) D_1}{2 l_1} \left(1 - \frac{c_{10}}{c_{1\infty}} \right)^2 - \frac{m}{c_{1\infty}} Q(t), \quad [2.17]$$

$$\frac{d l_m}{d t} + \dot{\alpha} l_m = \frac{1}{c_{m\infty}} Q(t) \quad [2.18]$$

$\delta_1(t)$ and $\delta_m(t)$ are parameters of the model profiles (see Fig. 1) and $Q(t)$ is given by the expression

$$Q(t) = \frac{2}{\pi} k_a c_{1\infty}^m \delta_1(t) G_m \left(\frac{c_{10}(t)}{c_{1\infty}} \right) - k_d c_{m\infty} l_m(t)$$

where

$$G_m \equiv \int_0^{\pi/2} \left\{ 1 - \left[\frac{c_{10}}{c_{1\infty}} + \left(1 - \frac{c_{10}}{c_{1\infty}} \right) \sin \omega \right]^m \right\} d\omega$$

The above equations together with Eqs. [2.1] and [2.13] represent a complete set of seven equations for determining seven unknown functions: $\Gamma(t)$, $c_{10}(t)$, $c_{m0}(t)$, $l_1(t)$, $l_m(t)$, $\delta_1(t)$ and $\delta_m(t)$. In the absence of micelles this set of equations reduces to one ordinary differential equation of the first order i.e. Eq. [2.17] with $Q(t)=0$ and three algebraic equations: Eqs. [2.1], [2.14] and [2.13] with $c_{m\infty}=0$.

We have applied our theory for interpretation of dynamic surface tension data obtained in solutions of sodium dodecyl sulfate (SDS) by the maximum bubble pressure method^{2,10}. For that purpose we have solved numerically the respective set of equations in the absence and in the presence of micelles. We have used empirical adsorption isotherm of SDS obtained by Tajima¹¹. The time dependence of the bubble area was obtained from video records of the expansion of single bubbles. The best numerical fits are shown in Fig. 2, where the dynamic surface tension is plotted versus life-time of the bubbles corrected for the dead time. We have used three adjustable parameters for fitting the data obtained below

CMC (Fig. 2, curves a and b): Γ_0 , D_1 and the limiting area per molecule A_∞ . The latter is a parameter of the adsorption isotherm. The calculated values of A_∞ were close to the value $2.5 \times 10^{-15} \text{ cm}^2$ obtained by Tajima¹¹. We have obtained that the initial adsorption is not equal to zero and increases with surfactant concentration which seems reasonable. The calculated diffusivities D_1 were approximately equal to the expected value¹² $5.5 \times 10^{-6} \text{ cm}^2/\text{s}$. The data above CMC (Fig. 2, curves c and d) were fitted by means of two adjustable parameters: Γ_0 and k_d . We have obtained initial adsorptions greater than zero and $k_d \approx 70 \text{ s}^{-1}$. The latter value seems realistic and can be recognised as corresponding to the fast relaxation process of demicellization². Since the above approach is rather general other reaction schemes of micellization¹⁹ can be also used instead of Eq. [2.5].

3. INTERFACIAL RHEOLOGY

If a surfactant adsorption layer is subjected to an isotropic dilation the rate of total (macroscopic) dilatation $\dot{\alpha}$ is defined by Eq. [2.3]. We can define also respective microscopic (local) analogues: rate of the local dilatation $\dot{\varepsilon}$ and local dilatation ε

$$\dot{\varepsilon} = -\frac{1}{\Gamma} \frac{d\Gamma}{dt} = \frac{1}{a} \frac{da}{dt}, \quad \varepsilon = \int_0^t \dot{\varepsilon} dt, \quad [3.1]$$

where $a = 1/(\Gamma N_A)$ is the area per molecule (N_A is the Avogadro number). The macroscopic and microscopic deformations may not coincide in the case of soluble surfactants due to the adsorption of surfactant molecules during dilation of the interface. It is commonly adopted in the literature^{3,4} that the dilational viscous stress is proportional to the rate of dilation $\dot{\alpha}$. Hence, for small deformations one can write the basic rheological equation connecting the total stress τ with the deformation as a sum of an elastic and a viscous component in the form

$$\tau = E_G \varepsilon + \eta_d \dot{\alpha} \quad [3.2]$$

where $E_G = -d\sigma/d\ln\Gamma$ is the Gibbs elasticity and η_d is the surface dilatational viscosity. However, the surface viscosity is a property of the adsorption layer and should be related to the interactions between the adsorbed molecules, i.e. it should depend on the local deformation, ε , rather than on α . In other words the viscous stress should be proportional to the rate of local deformation $\dot{\varepsilon}$ instead to the total one $\dot{\alpha}$. This is the main idea of our local approach to interfacial rheology⁵. Hence, the basic rheological equation should read

$$\tau = E_G \varepsilon + \eta_d \dot{\varepsilon} \quad [3.3]$$

The new constitutive equation, Eq. [3.3], 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 $\dot{\varepsilon} \neq 0$* . Hence, the adequacy of the above two constitutive equations can be verified experimentally by stress relaxation experiments at $\dot{\alpha} = 0$.

In the case of pure low molecular surfactants the dilatational surface viscosity is practically equal to zero and both rheological equations reduce to

$$\tau = E_G \varepsilon = \Delta\sigma, \quad [3.4]$$

hence, the total stress is equal to the change of the interfacial tension $\Delta\sigma$.

In contrast to τ and $\dot{\alpha}$, the local deformation ε and the rate of local deformation $\dot{\varepsilon}$ are not directly measurable. The latter are connected to the total (macroscopic) deformation via the mass balance equation. We derived the following expressions for ε and $\dot{\varepsilon}$:

$$\varepsilon = \int_0^{t_A(t)} \exp\left[\frac{t_A(t) - \vartheta}{t_D}\right] \operatorname{erfc}\left[\sqrt{\frac{t_A(t) - \vartheta}{t_D}}\right] \frac{d}{d\vartheta} \left(\frac{A}{A_a} - 1\right) d\vartheta \quad [3.5]$$

$$\dot{\varepsilon} = \left(\frac{A}{A_a}\right)^2 \left[\frac{d}{dt} \left(\frac{A}{A_a} - 1\right) + \frac{\varepsilon}{t_D} - \frac{1}{t_D \sqrt{\pi}} \int_0^{t_A(t)} \sqrt{\frac{t_D}{t_A(t) - \vartheta}} \frac{d}{d\vartheta} \left(\frac{A}{A_a} - 1\right) d\vartheta \right] \quad [3.6]$$

where

$$t_A(t) = \int_0^t \left(\frac{A}{A_a} \right)^2 d\mathfrak{g} \quad \text{and} \quad t_D = \frac{1}{D} \left(\frac{d\Gamma}{dc} \right)_e^2 \quad [3.7]$$

are the normalized time and the characteristic diffusion time, respectively⁵. A_a is the mean area of the interface over the time interval t , but is not equal to the initial area $A(0)$, and the subscript "e" denotes an equilibrium value. Eqs. [3.5] and [3.6] have been derived for diffusion controlled adsorption assuming that initially the adsorption layer rests in equilibrium with surrounding bulk phases, the total deformation is small and the experimental time is not very large. The substitution of Eqs. [3.5] and [3.6] in Eq. [3.3] or in Eq. [3.2] yields an expression for the total stress as a function of time. The unknown parameters E_G , η_d , and t_D can be determined comparing the measured values of τ with the predicted by Eq. [3.3] or by Eq. [3.2] values by using a minimization procedure. In fact, only t_D is an adjustable parameter in such computations because there is only one pair E_G , η_d corresponding to a given t_D value.

In order to verify Eqs. [3.2] and [3.3] expansion-relaxation experiments have been performed^{5,6} by the expanding drop method^{5,6,13}. This method is based on the almost radial expansion of the surfactant adsorption layer formed on the surface of a drop attached to the tip of a capillary. The total stress τ is calculated from the capillary pressure and the radius of the almost spherical drop by means of the Laplace equation of capillarity. The capillary pressure is determined with a pressure sensor, while the drop radius is measured by means of a microscope and a video system.

The expansion - relaxation experiment performed by us can be divided in three periods: (i) an initial formation of a saturated surfactant adsorption layer at the interface keeping the drop area constant for several hours, (ii) an expansion of the adsorption layer increasing the drop area for several seconds and (iii) a relaxation of the expanded adsorption layer under a constant drop area. The total stress τ increases during drop expansion and reaches maximum just at the end of

expansion. Then its value gradually decreases due to the adsorption of more and more surfactant molecules on the interface at a constant drop area.

Gibbs elasticities E_G and characteristic diffusion times t_D calculated by means of Eq. [3.4] and [3.5] for drops of hexaoxyethylene dodecyl ether ($C_{12}E_6$) water solutions expanded in air are shown in Fig. 3 (the experimental points). In the same figure the values of E_G and t_D calculated from the surface tension isotherm¹⁴ are plotted (the lines in Fig. 3). As expected, the Gibbs elasticity E_G increases, whereas t_D decreases with increase of surfactant concentration, although the measured values of Gibbs elasticity are slightly lower than the calculated values. Similar trends of the dependencies of E_G and t_D on the surfactant concentration were observed for other low molecular surfactants⁶.

We have studied the influence of pH and the ionic strength on the rheological properties of bovine serum albumin (BSA) adsorption layers at decane/ water interface^{5,6}. The equilibrium surface pressure, $\pi = \sigma_0 - \sigma$ (σ_0 and σ are the interfacial tension at decane/ water and decane/ solution interface, respectively) was equal to 28 ± 0.5 dyn/cm in all experiments. It turned out that the values of the rheological parameters depend on the maximum total deformation α_{\max} reached in the experiments. A similar influence of the deformation on the surface elasticity modulus has been observed by Miller et al.¹⁵ for human albumin adsorption layers at decane/ water interface studied by square pulse relaxation technique. This can be due to the very high slope of the adsorption isotherm leading to nonlinearity effects already at very small deviations from equilibrium¹⁵ or to not purely diffusion-controlled adsorption mechanism of BSA as assumed by us. The latter hypothesis cannot be rejected in view of the findings of other researchers that the adsorption of BSA is diffusion controlled at low concentrations^{20, 21}. (Indeed, steric barrier against adsorption can be expected for higher concentrations of BSA.) Anyhow, the observed effect of α_{\max} needs further elucidation. In order to reveal the trends of E_G , η_d , and t_D with the change of pH we normalized their values by those obtained at pH = 5. This pH is very close to the isoelectric point of BSA, pI = 4.9. The results presented in Fig. 4 show that both surface elasticity E_G and relaxation time t_D

increase with increase of pH. The surface *dilatational viscosity* passes through a maximum at pH=6. A similar peak of the surface *shear viscosity* of BSA at pH=6 has been observed by Graham and Phillips¹⁷ at petroleum ether/ water interface and ionic strength 0.1 M. The results in Fig. 4 imply strong influence of the ionic strength on the rheological parameters. In general, the higher ionic strength suppresses the effect of pH. The tendencies for increase of E_G and t_D with increase of pH are less pronounced at higher ionic strength. The peak of η_d , at I=0.2 M is just hint, whereas it is very clear at ionic strength I=0.07 M. This may be due to more efficient screening of the charges in BSA molecules at the higher ionic strength, thus making the intermolecular interactions in the adsorption layer to be less sensitive toward change of the net molecular charge i.e. toward changes of pH. The magnitude of the rheological parameters also depend on the ionic strength. For instance, at pH=5 we have obtained $E_G=40$ dyn/cm, $\eta_d=49$ dyn.s/cm and $t_D=69$ s at I=0.07 M, but $E_G=18$ dyn/cm, $\eta_d=57$ dyn.s/cm and $t_D=281$ s at I=0.2 M. The values of E_G are comparable with those obtained for dichlorometane/ solution interface by means of compression experiments²⁰.

The comparison between the rheological equations [3.2] and [3.3] has shown, that the new equation [3.3] described slightly better the experimental data⁵. Both equations have given almost identical and realistic values for E_G , η_d and t_D of BSA adsorption layers and can be used for interpretation of expansion - relaxation experiments.

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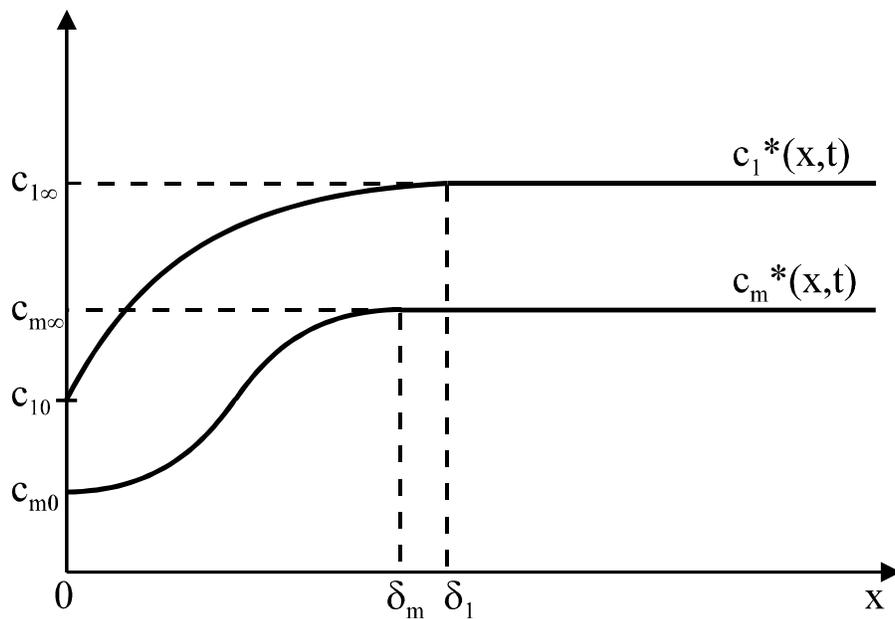


FIG. 1. Sketch of the model concentration profiles of free monomers, $c_1^*(x,t)$ and micelles, $c_m^*(x,t)$ (the air/water interface is located at $x = 0$).

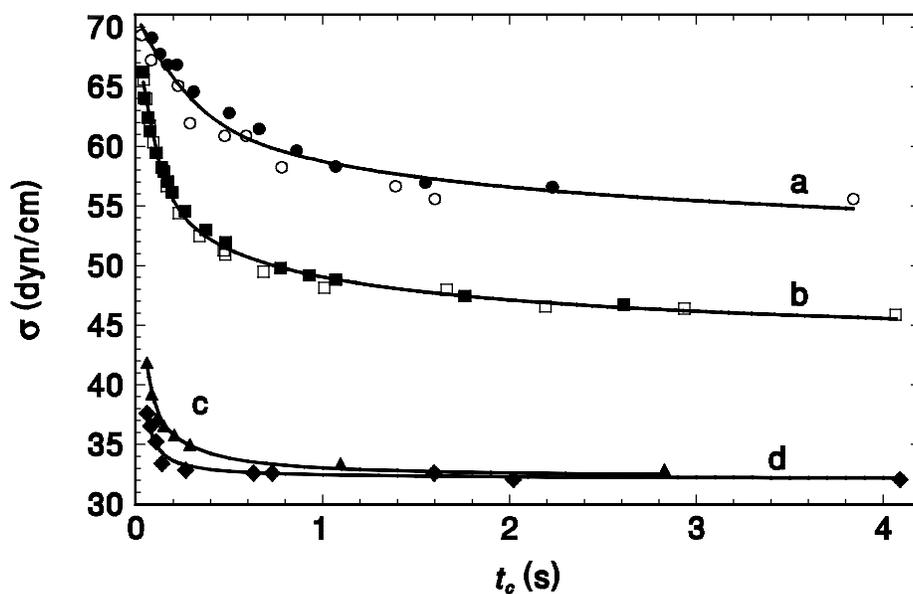


FIG. 2. Dynamic surface tension of submicellar (a, b) and micellar (c, d) SDS solutions at concentrations (in mol/l): 0.2×10^{-3} (a), 0.4×10^{-3} (b), 1.5×10^{-3} (c) and 2×10^{-3} (d) measured by the maximum bubble pressure method in the presence of 0.128 mol/l NaCl. Solid and empty figures correspond to different runs.

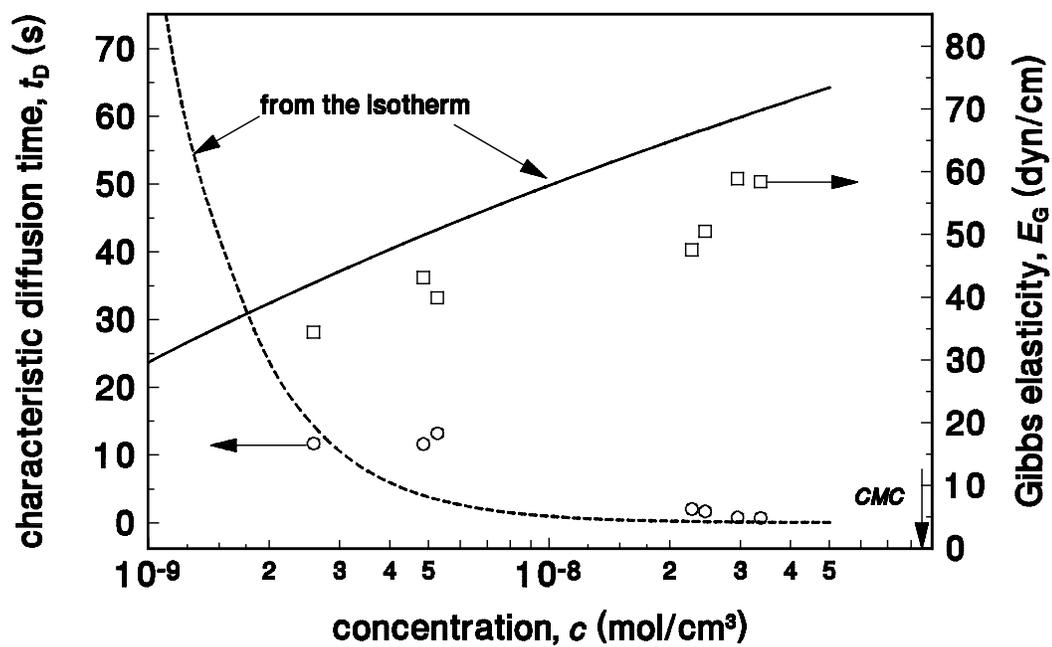


FIG. 3. Gibbs elasticity (boxes and full line) and characteristic diffusion time (circles and dashed line) of hexaoxyethylene dodecyl ether ($C_{12}E_6$) at water/ air interface versus surfactant concentration. The lines are calculated from the surface tension isotherm taken from Ref. (14) by means of the Gibbs equation for the adsorption.

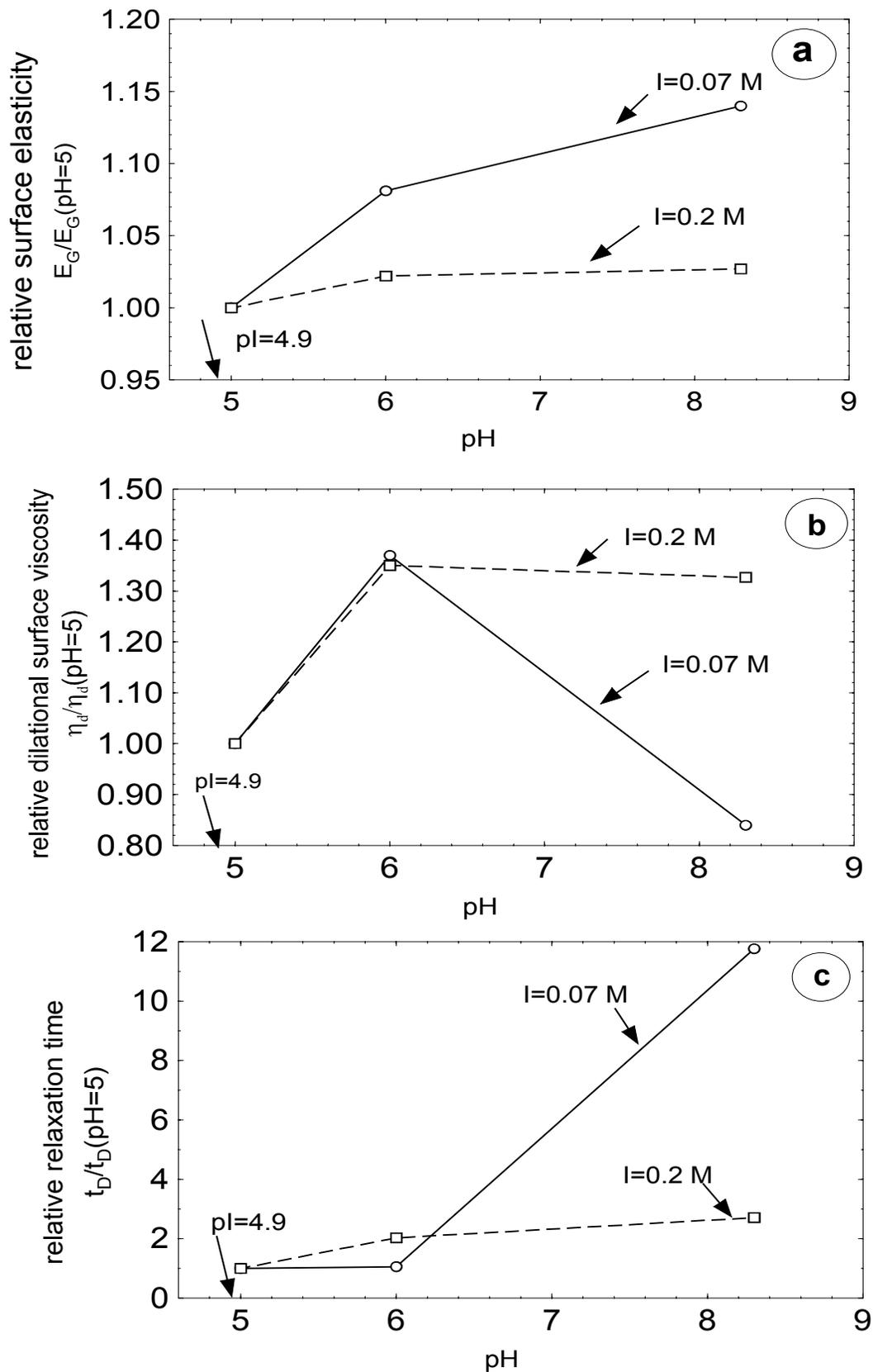


FIG. 4. Effect of pH (maintained by phosphate buffer) on the dilational surface elasticity (a), dilational surface viscosity (b) and characteristic relaxation time of BSA adsorption layers at n-decane/ water interface. $C_{\text{BSA}}=0.0125$ wt%. The ionic strength I is equal to 0.07 M (full line) and 0.2 M (dashed line) adjusted by NaCl.