

Influence of Ionic Surfactants on the Drainage Velocity of Thin Liquid Films

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The process of thinning of liquid films in the presence of ionic surfactants and background electrolytes is studied. The lubrication approximation is used to obtain the influence of spatial dynamic distribution of the different ions and the electric potential on the mobility of film interfaces and on the additional nonequilibrium part of the electrostatic disjoining pressure. The material properties of the interfaces (Gibbs elasticity and surface viscosity) are taken into account. The bulk and surface diffusivities of ionic species tend to restore the equilibrium and suppress the role of the Gibbs elasticity. The problem is linearized under the assumptions of small deviations of the adsorption and the concentration from their equilibrium values and of small Peclet number. In the case of plane parallel films an analytical solution is obtained. The correctness of the assumptions, widely used in the literature, of constant surface charge, of constant surface potential, and of the quasi-equilibrium approach is discussed. Numerical analysis of the governing equations shows that the ionic surfactants influence the film drainage in two ways. For small surfactants and background electrolyte concentrations the main effect is a reduction in surface mobility, which decelerates the drainage of the film. At high surfactant or salt concentrations the interfaces become tangentially immobile and then dynamic changes in the concentration, adsorption, electric charge, and middle plane potential affect the film thinning due to the change in the nonequilibrium part of the electrostatic disjoining pressure. © 2001 Academic Press

Key Words: influence of ionic surfactants; thin liquid films; drainage velocity; mobility of interfaces; disjoining pressure; background electrolyte.

1. INTRODUCTION

Surfactants play an important role in the dynamic properties of thin liquid films formed between emulsion droplets or foam bubbles (1–3). The lifetime of the films is one of the main quantitative parameters in the generalized interpretation of the Bancroft rule (4, 5) and the theory of simultaneous flocculation and coalescence in emulsion and foam systems (6–8). In practice, nonionic and ionic surfactants and background electrolytes

and their mixtures are used to stabilize or destabilize emulsions and foams (9, 10). Hence the detailed study of the surfactant influence on the velocity of film drainage is a starting point for many publications in the literature.

Detailed review of the publications concerning the drainage velocity of thin films is given in Refs. (1–5, 11). Mostly, the lubrication approximation is used to solve the mathematical problem arising from the physical model of the system (1, 2, 4, 11–16). This approximation is applicable not only to plane parallel films but also to films with deformed interfaces, dimples, and pimples (17).

The physical picture of the film thinning can be described schematically as follows: Under the action of an external force, the liquid flows out from the film to the meniscus, carrying away surfactant molecules from the bulk and the surface. These bulk and surface convective fluxes disturb the equilibrium distribution of the different ions, causing gradients in the bulk and the surface chemical potentials. Both surface and bulk diffusion fluxes arise to restore the equilibrium. In addition, the surface intermolecular attractive or repulsive forces (18, 19) strongly affect the whole process of film drainage when the film thickness is below 100 nm.

Even though the process of film thinning is widely investigated in the literature, there are few theoretical works that deal with the influence of ionic surfactants on that process. The role of the dynamic properties of ionic surfactants in the stability of equilibrium thin liquid films is discussed in Refs. (20, 21). The authors have used the so-called “quasi-equilibrium” approach, which assumes the equilibrium Boltzmann distribution of all ions in the whole process of evolution of fluctuations. Therefore the effect of ionic surfactants is accounted for only through the electric potential, which in that simplification does not depend on the radial coordinate, r . As was mentioned above, the film thinning disturbs the equilibrium distribution of the ions in both radial and vertical directions, causing bulk and surface diffusion fluxes. Hence, to illustrate the effect of ionic surfactants on the process of film thinning a detailed description of the dynamic of different ions is needed. To do so, together with the diffusion processes, one must specify the mechanism of adsorption of different ions to determine the surface electric charge. Following recent work on the thermodynamics of ionic surfactants, the

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effect of counterion binding must be taken into account (23–27). It is shown theoretically and experimentally (23–27) that the adsorption of counterions and the presence of electrolytes increase the adsorption of the surface active ions and interfacial elasticity and decrease the interfacial tension.

In this work we present a solution to the problem of drainage of a thin liquid film in the presence of ionic surfactants and background electrolytes. In Section 2 the mathematical model of the problem based on the lubrication approximation is formulated. The bulk and surface diffusion of all species and the surface elasticity and viscosity are taken into account. In the case of small deviation of surfactant concentrations and adsorptions from equilibrium the problem is linearized and the influence of surfactant is accounted for in the mobility of the interfaces (Section 3). Analytical treatment of the problem for plane parallel films is described in Section 4. Numerical results, given in Section 5, show the effects of surface mobility and the nonequilibrium part of the electric pressure on film drainage. Some concluding remarks are presented in Section 6.

2. MATHEMATICAL FORMULATION OF THE PROBLEM: LUBRICATION APPROXIMATION

The physical background of the influence of ionic surfactants on the drainage process of thin liquid films can be expressed in the following schematic way. When the film interfaces approach each other, the liquid flows toward the meniscus and carries away the surfactant molecules (Fig. 1). The surface velocity, \mathbf{u} , creates surface convective fluxes of the i th ion, $\mathbf{j}_{i,c} = \Gamma_i \mathbf{u}$ (Γ_i is the nonequilibrium adsorption), which generate gradients of the surface electrochemical potentials, $\mu_{i,s}$ ($i = 1, \dots, n$). Due to these gradients, the reverse surface electrodiffusion fluxes, $\mathbf{j}_{i,s}$, tend to restore the equilibrium (Fig. 1). Similarly, the gradients in the bulk electrochemical potentials, μ_i , produce bulk electrodiffusion fluxes, \mathbf{j}_i , which oppose the bulk convective trans-

port, $c_i \mathbf{v}$ (c_i is the nonequilibrium concentration of surfactants and \mathbf{v} is the bulk velocity). The characteristic time of the adsorption processes is much less than the time of film drainage. Therefore, it can be assumed that the surface electrochemical potentials are equal to the subsurface bulk electrochemical potentials; hence the nonequilibrium adsorptions, Γ_i , and the subsurface concentrations, $c_{i,s}$, are related through the general adsorption isotherms $\Gamma_i = \Gamma_i(c_{1,s}, c_{2,s}, \dots, c_{n,s})$. These produce additional differences between the electrochemical potentials close to the interfaces and in the middle plane of the film, which are compensated by the component of bulk electrodiffusion fluxes directed towards the interfaces (Fig. 1).

The process of adsorption of ionic surfactants on the film interfaces is accompanied by an increase in the surface electric potential, ψ_s , and the charge density, q_s . In its own turn, the presence of surface electric potential is related to the formation of a diffuse electric double layer (EDL) inside the film. The charged surfaces repel the newcoming surfactant molecules (Fig. 1), which results in deceleration of the adsorption process. The diffusion transport of the surface active ions, counterions, and coions is strongly affected by the electric field in the diffuse EDL. It is important to note that the electric double layer in the vicinity of an adsorption monolayer of ionic surfactant contains a Stern layer and a diffuse electric double layer (see Fig. 1 in Ref. 23). The Stern layer consists of adsorbed counterions, whereas the diffuse layer contains free ions involved in Brownian motion. Near the charged surfaces there is an accumulation of counterions and a depletion of coions. In the zone where the diffuse EDLs of the two film interfaces overlap, the electric potential distribution changes and influences the diffusion processes in the gap region. Herein the term EDL refers to the diffuse EDL.

The nonuniform surfactant distribution along the surface leads to variations in the local value of the surface tension, σ , which brings about the surface elastic force (Gibbs elasticity). On the other hand, the adsorption layer and the EDL may undergo dilatational and shear deformations during motion, which produce surface viscous stresses. Finally, the surface elements are under the action of the bulk stress caused by the liquid flow and by the electric potential distribution in the film. If the film is relatively thin, the intermolecular forces also affect the drainage through the disjoining pressure, Π . For slow motion (low Reynolds number) the intermolecular, electric, and viscous forces counterbalance the driving force, F , at every given moment, t .

In the present work we investigate the drainage process of a symmetric thin liquid film, formed between two drops or bubbles, which is stabilized by a mixture of nonionic and ionic surfactants and a background electrolyte. The problem is described in a cylindrical coordinate system, Orz , where the droplet interface, S , is defined by $z = H(t, r)/2$ and H is the local film thickness. In addition we will consider only axially symmetric flows, in which none of the parameters depend on the meridian angle. The middle plane is $z = 0$ and the unit normal at the surface S pointed to the drop phase is \mathbf{n} . The common solution to

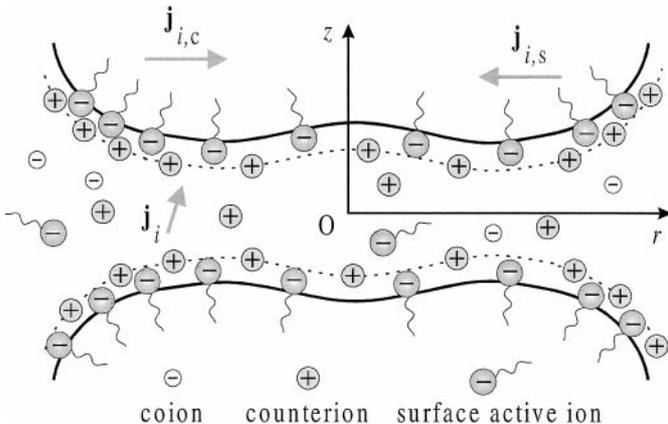


FIG. 1. Schematic picture of a thin liquid film stabilized by ionic surfactant. The ion bulk and surface diffusion fluxes are respectively \mathbf{j}_i and $\mathbf{j}_{i,s}$. The surface convective flux is $\mathbf{j}_{i,c}$.

such problems (1, 2, 4, 11–17) is to use the lubrication approximation. The general assumptions for this approximation are (i) *small Reynolds number*, (ii) *small film thickness* compared to the characteristic drop radius, and (iii) *small slope of the interfaces*.

The film between the drops is stabilized by a mixture of nonionic and ionic surfactants and the background electrolyte (salt). To find the surfactant distribution of the different ions we employ the following assumptions, which are widely used in the literature (1, 2, 4): (iv) *small Peclet number* in the gap and (v) *surfactants and salt are soluble only in the continuous (film) phase* (in this case the viscous friction from the fluid in the droplets is negligible compared to the friction from the continuous phase—the emulsion system behaves as a foam—see Ref. 4).

Under these assumptions the governing equations are formulated in the following subsections.

2.1. Mass Balance of Components and Electric Potential Distribution

The changes in the concentrations of the different species in the bulk are compensated by the convective, $c_i \mathbf{v}$, and the bulk electrodiffusion, \mathbf{j}_i , fluxes:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{v} + \mathbf{j}_i) = 0, \quad i = 1, \dots, n, \quad [1]$$

$$\mathbf{j}_i = -D_i \left(\nabla c_i + c_i \frac{z_i}{kT} \nabla \psi \right), \quad i = 1, \dots, n. \quad [2]$$

Here ψ is the electric potential in the bulk, k is the Boltzmann constant, T is the temperature, D_i is the bulk diffusion coefficient, and z_i is the electric charge of the ionic components. The second term in the definition of the bulk diffusion flux [2] represents the so-called “electromigration” term, which accounts for the influence of the EDL on the diffusion process of different ions. The two-dimensional analogue of Eq. [1] is the mass balance equation of the surfactant species at the film interface,

$$\frac{\partial \Gamma_i}{\partial t} + \nabla_s \cdot (\Gamma_i \mathbf{u} + \mathbf{j}_{i,s}) = \mathbf{n} \cdot \mathbf{j}_i, \quad i = 1, \dots, n, \quad [3]$$

where ∇_s is the surface gradient operator (2) and $\mathbf{n} \cdot \mathbf{j}_i$ is the bulk electrodiffusion flux from the contiguous bulk phase to the interface.

After integrating Eq. [1] from 0 to $H/2$ with respect to z , using the kinematic boundary condition at the film interface, and summing the result with Eq. [3], we obtain the integrated mass balance of each species:

$$\begin{aligned} \frac{\partial}{\partial t} \left(\Gamma_i + \int_0^{H/2} c_i dz \right) &= -\frac{1}{r} \frac{\partial}{\partial r} \\ &\times \left\{ r \left[\Gamma_i u + J_{i,s} + \int_0^{H/2} (c_i v_r + J_i) dz \right] \right\}, \quad i = 1, \dots, n. \end{aligned} \quad [4]$$

Here v_r and u are the radial components of the bulk and surface velocities, and J_i and $J_{i,s}$ are the radial components of the bulk and surface electrodiffusion fluxes, respectively. Equation [4] expresses the fact that the local change in the mass of the molecules across the film is compensated by the bulk and surface convective and diffusion fluxes (see Fig. 1).

In the case of lubrication approximation and for small Peclet numbers, the leading order of the diffusion equations [1], [2] becomes

$$\frac{\partial c_i}{\partial z} = -c_i \frac{z_i}{kT} \frac{\partial \psi}{\partial z}, \quad i = 1, \dots, n. \quad [5]$$

The solution to Eq. [5] gives the leading order of the nonequilibrium concentration in the bulk phase, c_i . It obeys a distribution, similar to the Boltzmann type:

$$\begin{aligned} c_i &= c_{i,m} \exp \left[-\frac{z_i}{kT} (\psi - \psi_m) \right] \\ &\equiv c_{i,n} \exp \left(-\frac{z_i \psi}{kT} \right), \quad i = 1, \dots, n. \end{aligned} \quad [6]$$

Here $c_{i,m}(t, r)$ and $\psi_m(t, r)$ are the concentration and the electric potential in the middle plane $z = 0$, respectively. The concentration, $c_{i,n}(t, r) \equiv c_{i,m} \exp[z_i \psi_m / (kT)]$, can be interpreted as the limit of the concentration when the electric potential, ψ , goes to zero. In the case of nonionic surfactant solution ($z_i = 0$), $c_{i,n}(t, r)$ is exactly the concentration of the nonionic components at the middle plane. Our model is distinguished from the quasi-equilibrium approach used in Refs. (20, 21), which assumes that $c_{i,n}(t, r)$ is a constant and its value is equal to the concentration of the species at infinite distance from the interface, $c_{i,\infty}$. Due to this assumption the formal limit $\psi \rightarrow 0$ made from the results in Refs. (20, 21) does not give the simple results for nonionic surfactants (4) where the surfactant concentrations, $c_{i,n}$, may depend significantly on t and r in the process of film thinning.

We use the subscripts “m” and “s” to indicate that the respective values of the different physical parameters are calculated in the middle plane and on the surface, respectively. The subscript “n” refers to the value of the variables in the case of nonionic surfactant, which can be derived when the formal limit $\psi \rightarrow 0$ is performed.

Using Eqs. [2], [5], and [6] the leading order of the radial component of the bulk diffusion flux, J_i , appearing in the integrated mass balance equation [4], can be rewritten in the form

$$\begin{aligned} J_i &= -D_i \left(\frac{\partial c_i}{\partial r} + \frac{z_i c_i}{kT} \frac{\partial \psi}{\partial r} \right) \\ &= -D_i \exp \left(-\frac{z_i \psi}{kT} \right) \frac{\partial c_{i,n}}{\partial r}, \quad i = 1, \dots, n. \end{aligned} \quad [7]$$

Therefore, the quasi-equilibrium approach ($c_{i,n} = c_{i,\infty}$, where $c_{i,\infty}$ is the concentration of the i th ion at infinity distance from the

interface) does not take into account the bulk diffusion processes of the different ions.

To define the surface diffusion fluxes we must specify the mechanism of adsorption. It was proven in the literature (1, 25–27) that for the process of film thinning the mechanism of adsorption is diffusion controlled. From a thermodynamic viewpoint it follows (23, 24) that the electrochemical surface potential of each species, $\mu_{i,s}$, is equal to the electrochemical bulk potential in the contiguous layer (the boundary between the Stern and the diffuse EDL; see Ref. 23). Hence, from the general definitions of the surface diffusion flux (28, 29) and the electrochemical potential (23, 24), and from the leading-order concentration distribution [6] the following simple relationship is obtained:

$$J_{i,s} = -\frac{D_{i,s}\Gamma_i}{kT} \frac{\partial \mu_{i,s}}{\partial r} = -\frac{D_{i,s}\Gamma_i}{c_{i,n}} \frac{\partial c_{i,n}}{\partial r}, \quad i = 1, \dots, n. \quad [8]$$

Here $D_{i,s}$ is the surface diffusion coefficient. For the same reason, as was mentioned before, the quasi-equilibrium approach (20, 21) does not account for the influence of the surface diffusion on the film drainage (in this approach $J_{i,s} = 0$). The formal limit for one nonionic component in Eq. [8] gives the expression for the surface diffusion flux widely used in the literature (1, 2, 4, 11).

The electric potential, ψ , is related to the bulk charge density, q , through the well-known Poisson equation. In the lubrication approximation it is written as

$$\frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi}{\varepsilon} q = -\frac{4\pi}{\varepsilon} \sum_{i=1}^n z_i c_i, \quad [9]$$

where the dielectric permittivity is ε . If the Boltzmann-type distribution [6] is substituted into Eq. [9] and the resulting equation is integrated with respect to z , the following first integral can be obtained:

$$\left(\frac{\partial \psi}{\partial z}\right)^2 = \frac{8\pi kT}{\varepsilon} \sum_{i=1}^n (c_i - c_{i,m}). \quad [10]$$

The condition for electroneutrality of the solution as a whole is equivalent to the Gauss law, which determines the surface charge density, q_s . In the lubrication approximation it reads (23)

$$\frac{\partial \psi}{\partial z} = \frac{4\pi}{\varepsilon} q_s = \frac{4\pi}{\varepsilon} \sum_{i=1}^n z_i \Gamma_i \quad \text{at } z = H/2. \quad [11]$$

The assumption for diffusion-controlled adsorption allows us to close the system of equations [1]–[11] with the respective isotherms for the different species, $\Gamma_i = \Gamma_i(c_{1,s}, c_{2,s}, \dots, c_{n,s})$. Usually (23, 24) the coions do not adsorb in the Stern layer and their adsorptions are practically zero. The list of commonly encountered isotherms is given in a recent work (23). Therefore, if we know the velocity distribution, the problem of the concentrations, the adsorptions, and the electrical potential distributions is completed.

2.2. Integrated Bulk Continuity Equation, Tangential Stress Balance, and Force Balance

In the case of a multicomponent ionic liquid mixture the density of the electric force, $q\mathbf{E}$ ($\mathbf{E} = -\nabla\psi$ is the electric field), plays the role of a spatial body force in the well-known Navier–Stokes equation of motion (30). In the lubrication approximation the radial and vertical components of the momentum balance equation are simplified to

$$\frac{\partial p}{\partial r} + \sum_{i=1}^n z_i c_i \frac{\partial \psi}{\partial r} = \eta \frac{\partial^2 v_r}{\partial z^2}, \quad [12a]$$

$$\frac{\partial p}{\partial z} + \sum_{i=1}^n z_i c_i \frac{\partial \psi}{\partial z} = 0. \quad [12b]$$

The dynamic viscosity and the dynamic pressure are denoted by η and p , respectively. After substituting the expression for the leading-order surfactant distribution [6] into Eq. [12b] and integrating the result, we derive the following expression for the pressure distribution:

$$p = p_m + kT \sum_{i=1}^n (c_i - c_{i,m}) \equiv p_n + kT \sum_{i=1}^n (c_i - c_{i,n}). \quad [13]$$

Here $p_m(t, r)$ and $p_n(t, r)$ are the pressures in the middle plane and in the limiting case of nonionic surfactant solution when $\psi \rightarrow 0$, respectively. It is seen that the pressure in the continuous phase, p , depends on the vertical coordinate, z , only through its osmotic part generated from the electric potential.

The substitution of Eqs. [6] and [13] into the radial component of the momentum balance equation [12a] leads to the following expression for the radial component of the velocity:

$$\eta \frac{\partial^2 v_r}{\partial z^2} = \frac{\partial p_n}{\partial r} + kT \sum_{i=1}^n \left[\exp\left(-\frac{z_i \psi}{kT}\right) - 1 \right] \frac{\partial c_{i,n}}{\partial r}. \quad [14]$$

The last term in the right-hand side of Eq. [14], which represents the electric force, is a complex function of the vertical coordinate, z . It is important to note that in the quasi-equilibrium approach ($c_{i,n} = c_{i,\infty}$) (20, 21) this term is equal to zero. This shows that under the quasi-equilibrium approach (20, 21) the electric force appears as a potential force in the momentum balance equation. Therefore, this model is equivalent to the so-called “body force approach” (22) and the effects of the ionic surfactants on the film drainage and stability are accounted for only through the classical electrostatic part of the disjoining pressure.

To simplify all equations below we introduce new functions, m_{ik} , which are defined as

$$m_{i0} = \exp\left(-\frac{z_i \psi}{kT}\right) - 1,$$

$$m_{ik} = \frac{2}{h} \int_0^z m_{i,k-1} dz \quad i = 1, \dots, n, \quad k = 0, \dots, 3, \quad [15]$$

where h is the minimal thickness of the film. Hence, using Eqs. [14] and [15], the condition for the symmetry of the film with respect to the middle plane, and the kinematic boundary condition at the film surface, one can calculate the distribution of the radial component of the velocity as

$$v_r = u + \frac{4z^2 - H^2}{8\eta} \frac{\partial p_n}{\partial r} + \frac{kTh^2}{4\eta} \sum_{i=1}^n (m_{i2} - m_{i2,s}) \frac{\partial c_{i,n}}{\partial r}, \quad [16]$$

where $m_{i2,s}$ is the value of the function m_{i2} calculated at the film surface $z = H/2$. In the case of nonionic surfactants $m_{ik} = 0$ and Eq. [16] gives the corresponding expression for the velocity in Ref. (12).

To close the system of equations for fluid motion, the tangential stress boundary condition and the force balance equation are used. The boundary condition for the balance of the surface excess linear momentum takes into account the influence of the surface tension gradient (Marangoni effect), surface viscosity (Boussinesq effect), and the electric part of the bulk pressure stress tensor (see Refs. 23, 30). In the lubrication approximation the tangential stress boundary condition at the interface, using Eqs. [13] and [16], is simplified to

$$\begin{aligned} & \frac{H}{2} \frac{\partial p_n}{\partial r} + kT \frac{h}{2} \sum_{i=1}^n m_{i1,s} \frac{\partial c_{i,n}}{\partial r} + q_s \frac{\partial \psi}{\partial r} + \frac{2\pi}{\varepsilon} q_s^2 \frac{\partial H}{\partial r} \\ & = \frac{\partial \sigma_a}{\partial r} + \eta_s \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial (ru)}{\partial r} \right]. \end{aligned} \quad [17]$$

The surface viscosity η_s is the sum of the interfacial shear and dilational viscosities. The gradient of the interfacial tension in Eq. [17] is calculated using only the adsorption part of the interfacial tension, σ_a , because the diffuse electric part of σ is already included in the electric part of the pressure tensor (see Ref. 23). The formal limit ($\psi \rightarrow 0$) transforms Eq. [17] into the tangential stress boundary condition for nonionic surfactants used in Refs. (1, 2, 4, 11–14).

The film between the bubbles thins due to the action of the external force, F , which for small Reynolds number is balanced by the hydrodynamic drag force and the intermolecular forces. Hence, in the lubrication approximation we obtain.

$$\begin{aligned} F &= 2\pi \int_0^\infty (p_m + \Pi_{nel} - p_\infty) r \, dr \\ &= 2\pi \int_0^\infty \left[p_n + kT \sum_{i=1}^n (c_{i,m} - c_{i,n}) + \Pi_{nel} - p_\infty \right] r \, dr, \end{aligned} \quad [18]$$

where p_∞ is the pressure at infinity in the meniscus region and Π_{nel} is the disjoining pressure which takes into account all nonelectric types of intermolecular interactions [van der Waals, steric, etc., except the electrostatic disjoining pressure component (18, 19)].

If the surface equation of state (dependence of the interfacial tension, σ , on the adsorption), the adsorption isotherms, and the film profile, H , are known, the model given above describes the physical picture of the film drainage. If the normal balance equation is included, the model can be applied also to investigation of the long-wave stability of films (31).

3. SMALL DEVIATIONS OF ADSORPTION AND SURFACTANT CONCENTRATION FROM EQUILIBRIUM

The problem described in Section 2 has no analytical solution for ionic surfactants nor for nonionic surfactants due to the strong nonlinear dependence of the interfacial tension and adsorption on the subsurface concentration. To overcome this difficulty in the literature (1, 2, 4, 11–15) the assumption of small deviations of the adsorption and the concentration from their equilibrium values is used. Then the electric potential ψ , the adsorption Γ_i , and the concentrations c_i and $c_{i,n}$ are presented as a sum of their equilibrium values (corresponding to zero velocity and denoted with subscript “e”) and small deviations from this basic state are denoted by δ :

$$\begin{aligned} \psi &= \psi_e + \delta\psi, \quad \Gamma_i = \Gamma_{i,e} + \delta\Gamma_i, \quad c_i = c_{i,e} + \delta c_i, \\ c_{i,n} &= c_{i,\infty} + \delta c_{i,n}, \quad i = 1, \dots, n. \end{aligned} \quad [19]$$

It is important to note that the equilibrium values, $\Gamma_{i,e}(H)$, $c_{i,e}(H, z)$, and $\psi_e(H, z)$, depend on the vertical coordinate, z , and on the local film thickness, H , because of the overlapping of both EDLs. The equilibrium values of concentrations obey the classical Boltzman law (23)

$$c_{i,e} = c_{i,\infty} \exp\left(-\frac{z_i \psi_e}{kT}\right), \quad i = 1, \dots, n. \quad [20a]$$

The electric potential at equilibrium, ψ_e , is a solution of the Poisson equation (see the particular case of Eq. [10] at equilibrium)

$$\begin{aligned} \left(\frac{\partial \psi_e}{\partial z}\right)^2 &= \frac{8\pi kT}{\varepsilon} \sum_{i=1}^n c_{i,\infty} \\ &\times \left[\exp\left(-\frac{z_i \psi_e}{kT}\right) - \exp\left(-\frac{z_i \psi_{em}}{kT}\right) \right], \end{aligned} \quad [20b]$$

with the respective boundary condition for the conservation of the charge (see the Gauss law, Eq. [11]). The appropriate adsorption isotherms close the equilibrium problem [20]. Through the vertical distribution of the electric potential all parameters depend on the local film thickness, H . The subscript “m” indicates that the respective value of the physical parameter is calculated in the middle plane.

The transformation of the integrated mass balance equation of the surfactant species [4] into a linear form is the first important simplification of the problem in the case of small deviations

from equilibrium. If the expansions [19] and the relationships for the diffusion fluxes [7] and [8] are substituted into Eq. [4], the final form of the mass balance equations can be derived:

$$\frac{\partial}{\partial t} \left(\Gamma_{i,e} + \int_0^{H/2} c_{i,e} dz \right) + \frac{1}{r} \frac{\partial}{\partial r} \times \left[r \left(\Gamma_{i,e} u + \int_0^{H/2} c_{i,e} v_r dz - D_{i,\text{eff}} \frac{\Gamma_{i,e}}{c_{i,\infty}} \frac{\partial \delta c_{i,n}}{\partial r} \right) \right] = 0. \quad [21a]$$

In Eq. [21a] the influence of the surface and bulk diffusion of surfactants is combined into one effective diffusion coefficient, $D_{i,\text{eff}}$, defined as

$$D_{i,\text{eff}} \equiv D_{i,s} + \frac{D_i}{\Gamma_{i,e}} \int_0^{H/2} c_{i,e} dz \quad i = 1, \dots, n. \quad [21b]$$

From the Boltzmann distribution [20a] and the definition [21b] it is seen that the influence of the bulk diffusivity on the surface active ions, which are repelled from the interface, is not so pronounced. But for counterions this effect may become significant. Usually, for nonionic surfactants the second term in [21b] is negligible (1, 4) and the effective diffusion coefficient is equal to the surface diffusion coefficient.

The time derivative in Eq. [21a] cannot be neglected because the equilibrium values of the adsorption, $\Gamma_{i,e}$, and the concentration of different ions, $c_{i,e}$, depend on the local film thickness, H , which changes during the process of film drainage. To illustrate this effect we calculated the adsorption, $\Gamma_{i,e}$, the subsurface potential, ψ_{es} , and the electric potential in the middle plane, ψ_{em} , for different values of the minimal film thickness, h . As an example we used the parameters of the surface tension and adsorption isotherms for a solution of sodium dodecyl sulfate (SDS) in the presence of NaCl. It is shown in the literature (23) that for this solution the Frumkin and Stern adsorption isotherms are the most appropriate:

$$(K_1 + K_2 c_{2,\text{es}}) c_{1,\text{es}} = \frac{\Gamma_{1,e}}{\Gamma_\infty - \Gamma_{1,e}} \exp\left(-\frac{2\beta\Gamma_{1,e}}{kT}\right), \quad [22a]$$

$$\frac{\Gamma_{2,e}}{\Gamma_{1,e}} = \frac{K_2 c_{2,\text{es}}}{K_1 + K_2 c_{2,\text{es}}}. \quad [22b]$$

Here index 1 is used for DS^- ions and index 2 corresponds to Na^+ , $\Gamma_\infty = 4.42 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ is the maximum possible surfactant adsorption corresponding to a close packing of the surfactant headgroups, $\beta = 0.4kT/\Gamma_\infty$ is the interaction parameter in the Bragg–Williams lattice model, and the constants $K_1 = 156 \text{ m}^3 \cdot \text{mol}^{-1}$ and $K_2 = 0.128 \text{ m}^6 \cdot \text{mol}^{-2}$ are related to the standard free energies of surfactant and counterion adsorption.

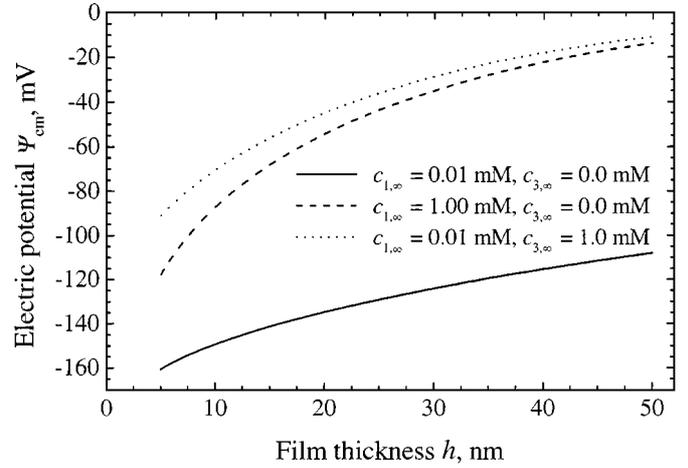


FIG. 2. Dependence of the electric potential in the middle plane on film thickness.

The influence of the film thickness, h , and the surfactant concentration on the equilibrium parameters is illustrated in Figs. 2–4. The electric potential in the middle plane, which gives the magnitude of the electrostatic part of the disjoining pressure, is negative and its absolute value increases when the distance between the interfaces decreases (see Fig. 2). The higher SDS concentration decreases the thickness of the EDL and the electrostatic part of the disjoining pressure goes down. The influence of the NaCl is similar. If the concentration of SDS is constant, then the increase in the salt concentration leads to a decrease in the absolute value of the electrostatic potential in the middle plane. For small capillary pressures the electrostatic component of the disjoining pressure may become large enough to balance the capillary pressure and the other nonelectric parts of the disjoining pressure. At that moment the film reaches its equilibrium thickness (18, 31). For that reason below we will assume that the capillary pressure is high enough to provide monotonous film thinning.

When ionic surfactant solutions are described in the literature (18), two simplifications are usually discussed: constant surface potential and constant surface charge. To illustrate the validity of these assumptions, we calculated the surface potential, ψ_s , and the relative change of the surface charge, $(\Gamma_{1,e} - \Gamma_{2,e})/(\Gamma_{1,e\infty} - \Gamma_{2,e\infty})$, as functions of the film thickness, where $\Gamma_{i,e\infty}$ is the equilibrium adsorption at an individual interface for the same concentration. Numerical results are plotted in Fig. 3. It is seen that at higher surfactant concentration the surface potential and the surface charge do not change significantly in the whole range of thicknesses greater than 5 nm; i.e., both hypotheses prevail. In contrast, at lower surfactant concentrations the surface potential changes from -145 to -165 mV and the relative change in the surface charge is about 50%. Therefore, neither hypothesis is valid for small concentrations, and the time derivative in Eq. [21a] cannot be neglected. The added salt decreases the thickness of the EDL and makes the

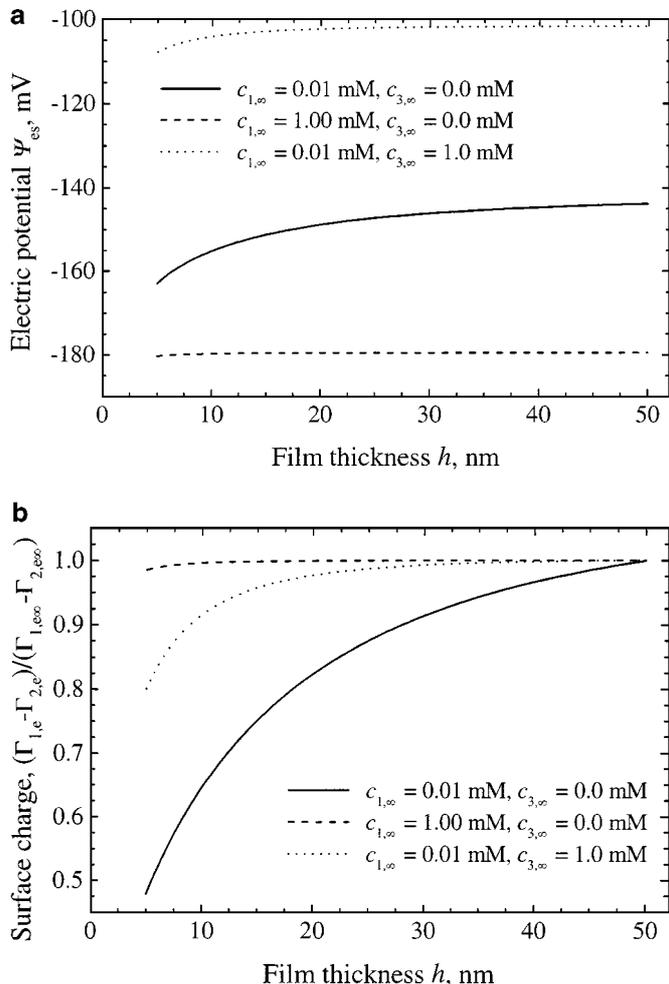


FIG. 3. Change in the surface potential (a) and in the surface charge (b) vs film thickness.

effect less pronounced. For example, for $c_{1,\infty} = 0.01$ mM and $c_{3,\infty} = 1.0$ mM the surface potential does not change significantly (see Fig. 3a). In contrast, the relative change in the surface charge for small film thickness is about 20% (see Fig. 3b). In this particular case the film thins in the regime of a constant surface potential.

In the mass balance equation [21a] the bulk and surface diffusivity are accounted for through the effective diffusion coefficient, $D_{i,\text{eff}}$. The values of the bulk diffusion coefficients we used are $D_1 = 5.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, $D_2 = 6.06 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, and $D_3 = 6.61 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (27). For our calculation we used the same values of the surface diffusion coefficients as the respective values of the bulk diffusion coefficients. In all cases we found that the effective diffusion coefficient of DS^- does not change considerably and is equal to the surface diffusion coefficient. In contrast, the effective diffusion coefficient of the counterion changes more than 100 times because of the role of the bulk diffusion (see Fig. 4). The lower the surfactant concentration, the larger the effective diffusivity of the counterion. The dependence on the film thickness is small. When the concentration of surfac-

tant becomes close to the critical micellar concentration, the effective diffusion coefficient of counterion is close to the surface diffusion coefficient. Therefore, the counterions tend to restore their quasi-equilibrium distribution much faster than the surface active ions.

The final step in completion of the system of equations is the reduction of the force balance equation [18] to the form

$$F_{\text{hd}} = 2\pi \int_0^\infty \left[p_n + kT \sum_{i=1}^n (\delta c_{i,m} - \delta c_{i,n}) - p_\infty \right] r dr, \quad [23a]$$

where the hydrodynamic drag force, F_{hd} , is defined as the difference between the driving force, F , and the total disjoining pressure calculated from the equilibrium parameters of the surfactant concentrations:

$$F_{\text{hd}} \equiv F - 2\pi \int_0^\infty \left[kT \sum_{i=1}^n (c_{i,\text{em}} - c_{i,\infty}) + \Pi_{\text{nel}} \right] r dr. \quad [23b]$$

The electrostatic disjoining pressure is calculated using the classical formula (see Eq. [23b] and Refs. 18 and 19). Therefore, in the case of small deviations of the adsorption and surfactant concentration from equilibrium, the ionic surfactants influence the hydrodynamic resistance through the mobility of the interface and the additional change of the dynamic pressure (see Eq. [23a]).

If the film profile, H , is known, applying the standard procedure described in Section 2 for linearization of the problem around the equilibrium adsorption, concentration, and potential reduces the system of equations to a linear problem for the parameters of the drainage flow. The coefficients of the linear problem are functions only of the equilibrium distribution of the electric potential and the film profile.

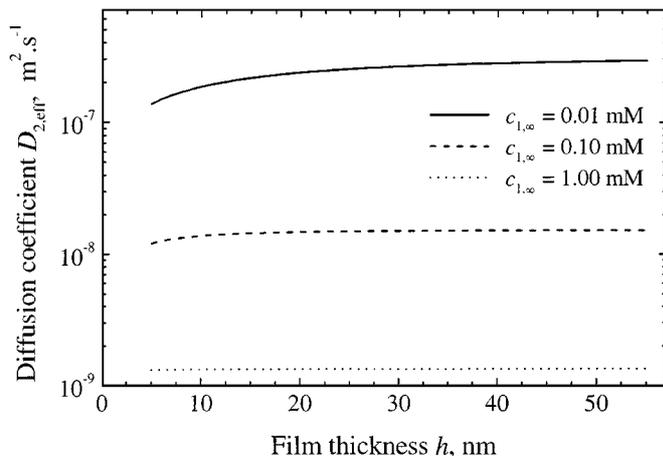


FIG. 4. Dependence of the effective diffusion coefficient, $D_{2,\text{eff}}$, on film thickness, calculated at three different surfactant concentrations in the absence of a background electrolyte.

4. INFLUENCE OF IONIC SURFACTANTS ON DRAINAGE VELOCITY OF PLANE PARALLEL FILMS

In Section 3 it was demonstrated that the influence of ionic surfactants becomes more pronounced when the EDLs of both interfaces overlap, i.e., for small film thicknesses. At these thicknesses the experimental results (3, 9, 10) show that the foam films have a uniform thickness, h , and they thin without significant change of the film radius, R . That is why we will focus below only on the case of plane parallel film thinning. Then the mobility parameter of the interfaces can be calculated from the model described in Sections 2 and 3.

To find the dimensionless numbers and characteristic measures for the parameters, the equation of continuity ($\nabla \cdot \mathbf{v} = 0$) is integrated along the z coordinate from 0 to $h/2$ with respect to the kinematic boundary condition and the solution for the radial component of the velocity [16]. In the resulting expression the expansion [19] is used to derive the final relationship

$$hu - \frac{h^3}{12\eta} \frac{\partial p_n}{\partial r} + \frac{kTh^3}{4\eta} \sum_{i=1}^n (m_{i3,es} - m_{i2,es}) \frac{\partial \delta c_{i,n}}{\partial r} = \frac{Vr}{2}, \quad [24]$$

where the drainage velocity of the film is $V = -dh/dt$. For the particular case of plane parallel films the surface velocity and the r derivatives of the pressure, concentration, and adsorption are proportional to the radial coordinate, r , as is also the case for nonionic surfactants (12). Therefore, the most convenient way to solve the problem is the introduction of the dimensionless amplitudes for the velocity, U , the pressure gradient, P , the potential and concentration gradients, $\Phi(z)$ and $C_i(z)$, and the adsorption gradient, G_i . These amplitudes are defined as

$$u \equiv \frac{Vr}{2h} U, \quad \frac{\partial p_n}{\partial r} \equiv -\frac{6\eta Vr}{h^3} P, \quad \frac{\partial \delta \psi}{\partial r} = \frac{6\eta Vr}{Ih^3 e} \Phi, \quad [25a]$$

$$\frac{\partial \delta c_i}{\partial r} = \frac{6\eta Vr}{kTh^3} C_i, \quad \frac{\partial \delta \Gamma_i}{\partial r} = \frac{6\eta Vr}{kTh^3} \frac{\Gamma_{i,e}}{I} G_i, \quad i = 1, \dots, n, \quad [25b]$$

where e is the elementary electric charge, Z_i and ξ_i are the valency and the molar fraction of i th ionic species, and I is the total bulk ionic strength of the solution defined as

$$I \equiv \frac{1}{2} \sum_{i=1}^n Z_i^2 c_{i,\infty}, \quad Z_i \equiv \frac{z_i}{e}, \quad \xi_i = \frac{c_{i,\infty}}{I}, \quad i = 1, \dots, n. \quad [25c]$$

Following the convention used in Sections 2 and 3, the dimensionless amplitude of the concentration gradients corresponding to the limit $\psi \rightarrow 0$ is denoted by $C_{i,n}$. The values of the dimensionless amplitudes of the concentration and the electric potential gradients in the middle plane and at the boundary between

the Stern and diffuse EDLs are $C_{i,m} \equiv C_i(0)$, $\Phi_m \equiv \Phi(0)$, and $C_{i,s} \equiv C_i(h/2)$, $\Phi_s \equiv \Phi(h/2)$, respectively.

After partial integration of the expression for the hydrodynamic force [23a] from 0 to the film radius, R , and after substitution of the definitions [25a] and [25b] into the resulting equation, the following relationship for the drainage velocity is derived:

$$\frac{V}{V_{Re}} = \left[P - \sum_{i=1}^n (C_{i,m} - C_{i,n}) \right]^{-1}, \quad V_{Re} \equiv \frac{2h^3 F_{hd}}{3\pi\eta R^4}. \quad [26]$$

In Eq. [26] V_{Re} , the Reynolds velocity, expresses the thinning rate of a planar film between two solid disks, i.e., for tangentially immobile film interfaces (32, 33). The influence of the equilibrium part of the disjoining pressure is included in the definition of the hydrodynamic force [23b]. Therefore, if the amplitudes are found, then the mobility parameter, V/V_{Re} , is known from Eq. [26].

If the definition [25] is substituted into Eq. [24] a simple relationship for the amplitudes is obtained:

$$U + P + 3 \sum_{i=1}^n (m_{i3,es} - m_{i2,es}) C_{i,n} = 1. \quad [27]$$

The linear form of the tangential stress boundary condition [17] is derived after using the expansion [19] and the definitions [25],

$$-P + \sum_{i=1}^n m_{i1,es} C_{i,n} + \frac{2q_{es}}{eIh} \Phi_s + \sum_{i=1}^n \frac{2E_i}{kTIh} G_i = 0, \quad [28a]$$

where E_i is the Gibbs elasticity of the interface corresponding to the change of the adsorption of i th species at equilibrium; i.e.,

$$E_i \equiv -\frac{\partial \sigma_{a,e}}{\partial \ln \Gamma_{i,e}} \quad i = 1, \dots, n. \quad [28b]$$

It is important to note that in the particular case of planar films the surface viscosity does not influence the drainage velocity of the films (1, 4). The effect of the surface viscous friction can be accounted for if the problem is solved for the meniscus and the film regions simultaneously (11, 14). Equations [27] and [28a] give the pressure and velocity amplitudes if all other amplitudes are known.

To obtain the values of the concentration amplitudes in the middle plane and at the surface, expansion [19] is substituted into the Boltzmann-type distribution [6] and the resulting equation is linearized around the equilibrium state. Using the definition for the dimensionless parameters the final result acquires the form

$$C_i = (C_{i,n} - \xi_i Z_i \Phi) \exp\left(-\frac{z_i \psi_e}{kT}\right), \quad i = 1, \dots, n. \quad [29]$$

Respectively, the linearization of the general adsorption

isotherms, $\Gamma_i = \Gamma_i(c_{1,s}, c_{2,s}, \dots, c_{n,s})$, around the equilibrium state gives

$$G_i = \sum_{k=1}^n b_{ik} \left(\frac{C_{k,n}}{\xi_k} - Z_k \Phi_s \right), \quad b_{ki} \equiv \frac{\partial \ln \Gamma_{k,e}}{\partial \ln c_{i,es}}, \quad [30]$$

where b_{ki} is the log–log slope of the equilibrium adsorption, $\Gamma_{k,e}$, with respect to the equilibrium subsurface concentration, $c_{i,es}$, $i, k = 1, \dots, n$. Equations [29] and [30] are used to calculate the adsorption and the concentration amplitudes in the middle plane and at the surface.

The amplitudes $C_{i,n}$ are calculated from the mass balance equation [21a]. The velocity distribution [16], simplified in the case of small deviations from equilibrium, is substituted into Eq. [21a] and the respective integrals are calculated. After long but trivial mathematical transformations the final dimensionless linear equation for the amplitudes reads

$$\begin{aligned} & \left(1 + m_{i1,es} + \frac{2\Gamma_{i,e}}{hc_{i,\infty}} \right) U + (1 + 3m_{i2,es} - 3m_{i3,es}) P \\ & + \sum_{k=1}^n n_{ik} C_{k,n} - \frac{24\eta D_{i,\text{eff}} \Gamma_{i,e}}{kTh^3 c_{i,\infty}^2} C_{i,n} \\ & = \frac{2}{c_{i,\infty}} \frac{d}{dh} \left(\Gamma_{i,e} + \int_0^{h/2} c_{i,e} dz \right), \quad i = 1, \dots, n. \end{aligned} \quad [31a]$$

Here the coefficients n_{ik} , which depend only on the equilibrium potential distribution, are calculated from the expressions

$$n_{ik} \equiv \frac{6}{h} \int_0^{h/2} (m_{i0,e} + 1)(m_{k2,e} - m_{k2,es}) dz \quad i, k = 1, \dots, n. \quad [31b]$$

Now only the values of the amplitudes for the electric potential in the middle plane and at the surface are unknown.

To obtain the linear form of the first integral [10] following from the Poisson equation the expansions [19] are substituted therein and the result is linearized around the equilibrium state:

$$\frac{\partial \psi_e}{\partial z} \frac{\partial \delta \psi}{\partial z} = \frac{4\pi kT}{\varepsilon} \sum_{i=1}^n (\delta c_i - \delta c_{i,m}). \quad [32a]$$

Using the linearized form of the Boltzmann-type distribution [6] after long mathematical transformations Eq. [32a] can be presented in the following complete differential form:

$$\begin{aligned} & 2 \sum_{i=1}^n (c_{i,e} - c_{i,em}) \frac{\partial}{\partial z} \left[(\delta \psi - \delta \psi_m) \left(\frac{\partial \psi_e}{\partial z} \right)^{-1} \right] \\ & = \sum_{i=1}^n (c_{i,e} - c_{i,em}) \left(\frac{\delta c_{i,n}}{c_{i,\infty}} - \frac{z_i \delta \psi_m}{kT} \right). \end{aligned} \quad [32b]$$

After integrating Eq. [32b] from 0 to $h/2$ and transforming the result in the dimensionless form using the definitions [25a] and [25b], we derive the relationship for the electric potential in the middle plane and at the surface:

$$\Phi_s = \Phi_m + \frac{\kappa^2 h^2}{8} \frac{q_{es}}{eTh} \sum_{i=1}^n g_i \left(\frac{C_{i,n}}{\xi_i} - Z_i \Phi_m \right). \quad [33a]$$

Here the coefficients, g_i , depend only on the equilibrium concentration distribution and are calculated from the expressions

$$g_i \equiv \frac{2}{h} \int_0^{h/2} (c_{i,e} - c_{i,em}) \left[\sum_{k=1}^n (c_{k,e} - c_{k,em}) \right]^{-1} dz, \quad i = 1, \dots, n. \quad [33b]$$

The inverse Debye screening length, κ , is defined by $\kappa^2 \equiv 8\pi e^2 I / (\varepsilon kT)$.

Finally, the Gauss law [11] linearized around the equilibrium state gives the connection between the amplitudes of the surface and middle-plane electric potential gradients:

$$\sum_{i=1}^n \left(C_{i,s} - C_{i,m} - \frac{\kappa^2 h^2}{2} \frac{q_{es}}{eTh} \frac{\Gamma_{i,e}}{hc_{i,\infty}} \xi_i Z_i G_i \right) = 0. \quad [34]$$

Solving the linear system of equations [27], [28a], [30], [31a], [33a], [34], and [29], written in the middle plane and at the boundary between the Stern and diffuse EDLs, the amplitudes of the adsorption, concentration, and electric potential are found. The problem cannot be simplified more because of the complex dependence of the coefficients on the equilibrium electric potential, ψ_e , and the film thickness, h . That is why in Section 5 the illustrated results are obtained numerically.

5. NUMERICAL RESULTS AND DISCUSSION

The experiments show that the surfactant and salt concentrations strongly affect the behavior of the thin liquid films (10, 34). To illustrate their influence on the process of film drainage we calculated the velocity of film thinning as a function of surfactant and salt concentrations for a real foam system stabilized by SDS in the presence of NaCl. All numerical calculations are performed for the values of surface and bulk diffusion coefficients and for the parameters of SDS isotherm given in Section 2. First we calculated V/V_{Re} vs concentration of SDS. The results are plotted in Fig. 5a. The curves correspond to three different salt concentrations: the solid line represents the case without salt, and the other two curves correspond to $c_{3,\infty} = 0.01$ mM and $c_{3,\infty} = 0.1$ mM NaCl, respectively. The film thickness is chosen to be $h = 20$ nm. The numerical results show that when the SDS concentration increases, the relative drainage velocity decreases, passes through a minimum, and then slightly

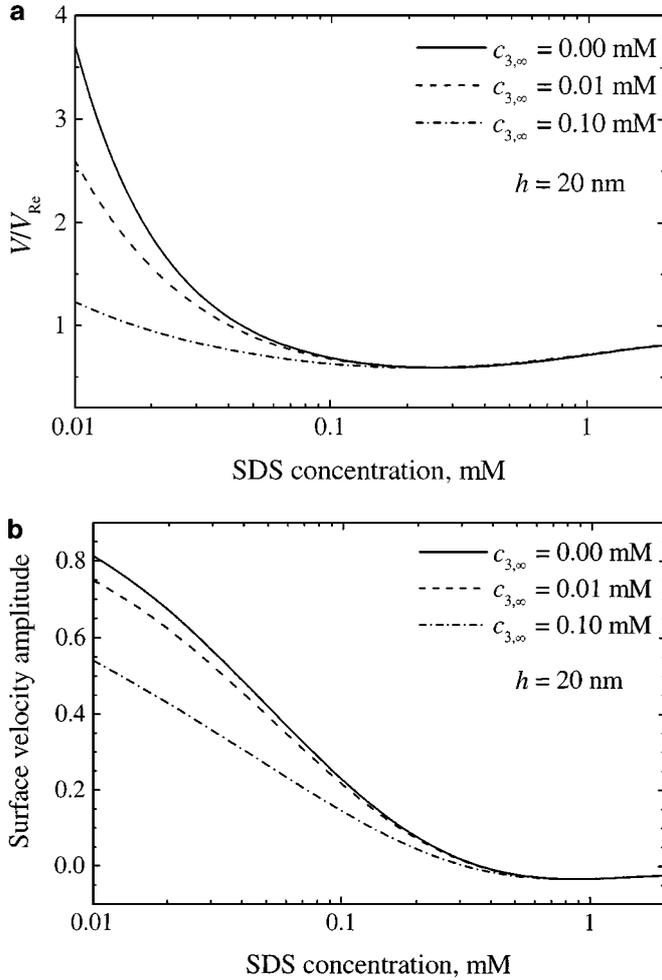


FIG. 5. Dependence of the mobility, V/V_{Re} (a) and of the amplitude of the surface velocity U (b) on surfactant concentration.

increases and tends to unity for high surfactant concentrations. The presence of background electrolyte slows down the drainage process and for $c_{3,\infty} = 0.1$ mM the velocity of film thinning is very close to the Reynolds velocity for the whole range of surfactant concentrations. From Fig. 5a it is seen that there is a region of surfactant concentrations in which the film thins with velocity lower than the Reynolds velocity. This fact will be explained more precisely in the discussions below. At low surfactant and salt concentrations the main effect is the reduction of the surface mobility with the increase of the surfactant concentration. This effect is confirmed by Fig. 5b, where the amplitude of the surface velocity, U , is plotted as a function of SDS concentration. The values of the film thickness, h , and salt concentrations, $c_{3,\infty}$, are the same as those in Fig. 5a. In closing, the surface velocity decreases with surfactant and salt concentrations. At a higher SDS concentration the surface velocity becomes negative. From a physical viewpoint this means that there is a small reverse surface convective flux from the meniscus region, which decelerates the film drainage. This flux arises from the different mobility of the surface active ions and

counterions (see the definition of the effective diffusion coefficients in Section 3). This flux brings new surfactant molecules back to the film in order to maintain the total charge density, thus creating additional dynamic pressure, which decelerates the film thinning.

The addition of salt leads to a decrease in relative drainage velocity and surface velocity. To explain this effect quantitatively, we calculated V/V_{Re} and U as a function of $c_{3,\infty}$, for three different values of surfactant concentration (see Fig. 6). The film thickness is kept constant, $h = 10$ nm. From Fig. 6a it is seen that at higher SDS concentrations, 0.05 and 0.1 mM, the relative velocity of thinning remains almost constant for the chosen range of salt concentrations, and for $c_{1,\infty} = 0.1$ mM the velocity of thinning is practically equal to the Reynolds velocity. It is important to note that in this case the surface velocity is not zero; i.e., the film surfaces are still tangentially mobile (see Fig. 6b). From Fig. 6b is also seen that the surface velocity decreases with increasing of NaCl concentration and remains almost constant at low salt concentrations. From the literature (23, 24) it is known that an increase in NaCl concentration

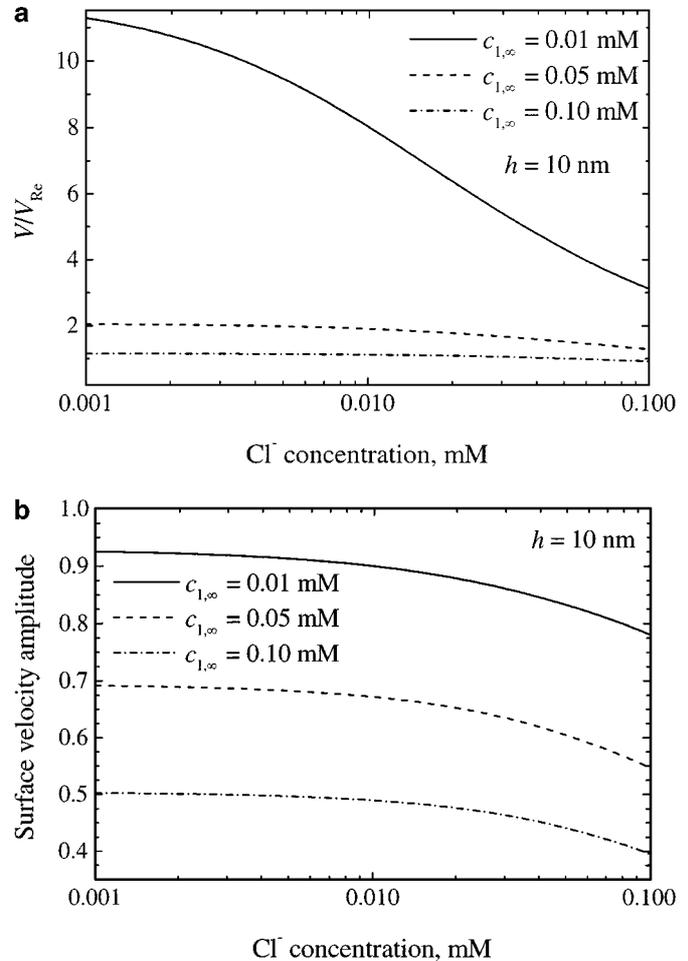


FIG. 6. Influence of the background electrolyte on mobility of the interfaces: (a) V/V_{Re} ; (b) amplitude of the surface velocity.

decreases the interfacial tension and favors adsorption of surfactant ions. This influence is more pronounced when the salt and surfactant concentrations have the same order of magnitude or when the NaCl concentration is higher. This is well demonstrated in Figs. 6a and 6b.

In the case of nonionic surfactants (1, 4, 12) the relative velocity is a linear function of $1/h$:

$$V/V_{\text{Re}} = 1 + b + h_s/h. \quad [35a]$$

Coefficients b and h_s account for the bulk and surface diffusivity. They are defined as

$$b = \frac{3\eta D}{E_G} \left(\frac{\partial c}{\partial \Gamma} \right)_e, \quad h_s = \frac{6\eta D_s}{kT\Gamma}. \quad [35b]$$

To check this dependence for ionic surfactants, the relative velocity vs film thickness is calculated in two ways: from the present model for ionic surfactants and by using Eq. [35]. The coefficients b and h_s for the nonionic surfactant model are calculated by adapting the surfactant isotherm for ionic surfactants to the Langmuir type—this way is widely used in the literature (35, 36). Thus the diffusion and adsorption processes in both models are accounted for and the differences between the results arise from additional osmotic pressure caused by the distribution of different ions (see Eq. [23a]). The results are plotted in Fig. 7a for two different sets of concentrations. The general trend follows behavior similar to that of nonionic surfactants—the larger the film thickness, the smaller the relative velocity and the more immobile the film interface. The functional dependence is different—for ionic surfactants the decrease in the surface mobility is much greater. The increase in surfactant concentration has a stabilizing effect. At large film thickness (about 100 nm) the curves corresponding to the nonionic model tend to $1 + b$, which corresponds to small interfacial mobility. For ionic surfactants the velocity of film thinning is smaller than V_{Re} . To investigate this behavior in more detail, the results for the amplitude of the surface velocity for the same surfactant concentrations are presented in Fig. 7b. For high surfactant concentrations the lower velocity can be related to the reverse surface convective fluxes. On the other hand, for small surfactant concentrations the effect of surface mobility cannot explain this tendency of the relative velocity. This is attributed to the very complex dynamic processes in the ionic species mass transport and electric potential distribution (see Fig. 7b).

In Fig. 8 the relative velocity, V/V_{Re} , and the amplitude of the electric potential in the middle plane are plotted as a function of SDS concentration. The NaCl concentrations are varied as 0.1, 1.0, and 10.0 mM and the film thickness is constant at 10 nm. The relative velocity is smaller than 1 in the whole range of surfactant concentration close to the critical micelle concentration. In all cases the surface mobility is not low. It is interesting to note that the minimum corresponds to $\kappa h \approx 1$. At a given

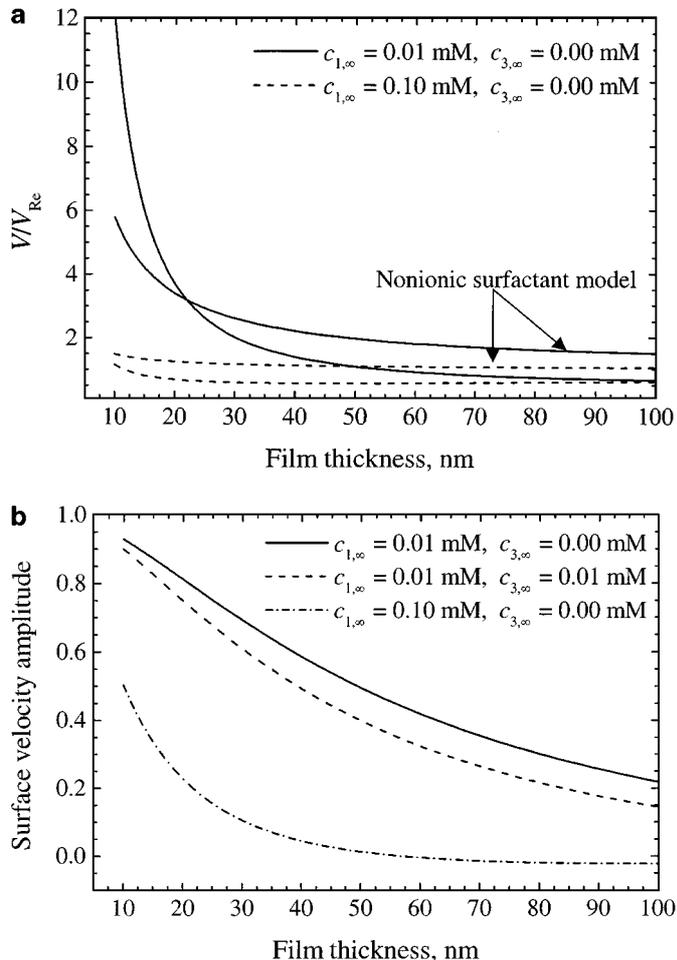


FIG. 7. V/V_{Re} (a) and the amplitude of the surface velocity (b) vs film thickness at different surfactants and salt concentrations.

NaCl concentration the amplitude of the electric potential in the middle plane does not change considerably (see Fig. 8b). When the concentration is low, both EDLs are fully overlapped and the bulk liquid flow carries away approximately the same number of ions in the whole film. Then the increase in the surfactant concentration decreases the interfacial mobility and the velocity profile becomes closer to the Poiseuille flow. The additional “dynamic disjoining pressure,” coming from the positive values of the electric potential amplitude in the middle plane, slows the film thinning. When the thickness of the EDL becomes smaller than the film thickness, the number of ions carried out from the drainage liquid flow is different for the surfactant ions and counterions. Their equilibrium values change considerably only close to the interface, and therefore their influence on the dynamic pressure in the whole film is not so pronounced; i.e., the film starts to drain more like the film stabilized by nonionic surfactants. Then the numbers of the surfactant ions and counterions carried out from the liquid flow in the middle plane become comparable; i.e., they are equivalent to the decreases in surfactant concentrations which, as it is illustrated in Fig. 2, increase

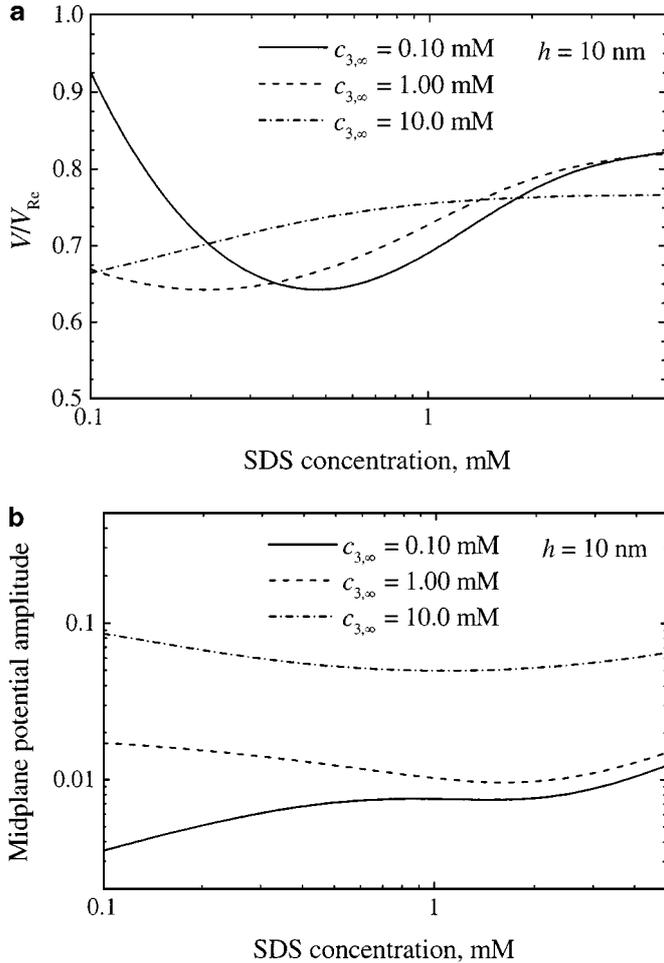


FIG. 8. Dependence of the relative velocity of thinning V/V_{Re} (a) and the amplitude of the electric potential in the middle plane (b) on surfactant and salt concentrations.

the electric potential in the middle plane. For that reason the relative velocity in Fig. 8a at SDS concentrations close to the critical micelle concentration of 5 mM is lower at higher NaCl concentrations. The difference between the Reynolds velocity and the calculated drainage velocity is exactly due to the change in the disjoining pressure (see Fig. 8b).

It is important to note that Figs. 5a–8a represent the ratio between the velocity of draining film, V , and the Reynolds velocity, V_{Re} . From Eqs. [23b] and [26] the influence of the disjoining pressure is included in the calculation of the Reynolds velocity. Therefore, the lifetime of the film, which depends on V , depends not only on the mobility parameter V/V_{Re} , but also on the magnitude of the Reynolds velocity, i.e., on the disjoining pressure itself.

6. CONCLUSIONS

A theoretical model for calculating the influence of ionic surfactants and background electrolytes on the drainage velocity of

thin liquid films is developed. This model takes into account the bulk and surface electrodiffusion fluxes of ions, which counterbalance the convection of species due to the bulk and surface liquid velocity. The resulting redistribution of ions leads to changes in bulk and surface charge density and electric potential. The interfacial rheology (surface elasticity and viscosity) is included in the model to show the role of the material properties of the interfaces.

In the case of small deviations of the adsorption and the surfactant concentration from their equilibrium values, the quasi-equilibrium part of the electrostatic interaction is included in the disjoining pressure, whereas the different mobilities of ions influence the interfacial elasticity. Thus, the resulting force represents the hydrodynamic driving force, which defines the hydrodynamic resistance of the film. The measure of the resistance is the ratio between the drainage velocity and the Reynolds velocity of film thinning. The influence of the surface and bulk diffusion is coupled in one effective diffusion coefficient, which shows that for the surface active ions the bulk diffusion is small compared to the surface diffusion. In contrast, the effect of the bulk diffusion on the mass transfer of counterions may play a dominant role.

The quantitative calculations for plane parallel films illustrate the main conclusions. The ionic surfactants and background electrolyte (salt) change the hydrodynamic resistance of the films in two ways—they reduce the surface mobility, and they change the dynamic pressure and the electric body force of the composition.

Increases in surfactant concentration and salt concentration increase surface elasticity. The interfacial mobility decrease and the films behave more like films between two rigid surfaces. This effect is more pronounced with changes in surfactant concentration. The background electrolyte favors adsorption of the surface active ions and decrease in the interfacial tension. Both the surface and bulk diffusion processes tend to restore the equilibrium, suppress the gradient of the interfacial tension, and make the interfaces more mobile. With the increase in the film thickness, the hydrodynamic friction in the vicinity of the interfaces decreases and the influence of the surface diffusion becomes less pronounced.

The complex dynamic processes of the mixture of ions cause changes in their concentrations in the bulk and at the surfaces. They produce dynamic variations of the bulk and surface charge and an additional dynamic effect on the electric force. Due to the dynamic part of the electric force and the charge variations, the dynamic pressure of the film increases and the drainage of the films slows down. Increases in surfactant and salt concentrations decrease the thickness of the diffuse electric double layer, and the dynamic electric interaction between two interfaces decreases. At high concentrations, the electric double layers are located mainly close to the interfaces and the effect of the additional deceleration of the film thinning is negligible.

The developed model can be also applied to investigations of the stability of the equilibrium thin liquid films.

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