EFFECT OF IONIC SURFACTANTS ON THE FILM DRAINAGE

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Abstract. *The drainage of a partially mobile thin liquid film between two deformed gas bubbles is studied. The lubrication approximation and the assumption for small Peclet number are used to formulate the mathematical model of the problem. The mass balance equations for each of the species (ionic surfactant and background indifferent electrolyte) are simplified to an integral mass balance equation in the film. The material properties of the surfaces (surface viscosity, Gibbs elasticity, surface and/or bulk diffusivities, and surface electric potential) are taken into account in the tangential and normal stress balances. A simple analytical solution for a plane-parallel film is derived in the case of small deviations from equilibrium. The numerical analysis of the governing nonlinear equations shows the region of transition from partially mobile to immobile interfaces. A quantitative explanation of the following effects is proposed: (i) the increase of the surface mobility with the bulk and surface diffusivities; (ii) the role of the surface viscosity, compared to that of the Gibbs elasticity; (iii) the significant influence of the meniscus on the film drainage due to the increased hydrodynamic resistance; (iv) the effects of the surface potential and disjoining pressure. The model can be applied to explain the stability of foams in practical applications.*

Keywords: *Ionic surfactant solution, Thin liquid film, Drainage velocity, Gibbs elasticity, Background electrolyte*

1. INTRODUCTION

The stability of emulsions and foams plays a crucial role in various chemical technologies. The collision of two emulsion droplets or foam bubbles may be accompanied by a deformation (flattening in the zone of contact) depending on the energy of interaction and hydrodynamic friction between them. In general, the gap between two fluid particles can be considered as a thin liquid film of uneven thickness. Hence, the detailed study of the surfactant influence on the velocity of film thinning is a starting point for many publications in the literature.

The problem for a slow buoyancy-driven motion of two viscous drops towards each other in pure liquids was investigated by Yiantsios & Davis (1990,1991). The authors studied the influence of the viscosity and the van der Waals intermolecular attractive force on the velocity of droplets approach. In most practical applications the emulsions and foams are stabilized by surfactant dissolved in the continuous phases. Due to the process of film thinning, the interfaces of the equilibrium surfactant solution are disturbed. The equilibrium is restored by adsorption from the bulk phase and by surface convection and diffusion, driven by the gradient of the interfacial tension (Marangoni effect) in interplay with the interfacial viscous friction (Boussinesq effect). Ivanov (1980) and Ivanov & Dimitrov (1988) proved that

the surface elasticity and viscosity strongly reduce the interfacial mobility and the viscous friction in the droplets is negligible (the emulsion system behaves as a foam). In addition, when the distance between the drops (bubbles) is small enough the intermolecular van der Waals, electrostatic, steric, and other surface forces become operative. These forces significantly change the film lifetime, i.e. the emulsion and foam stability. In addition, the meniscus decelerates the bubbles approach for small films (Danov *et al.*, 1999).

In various applications the bulk phase is a multi-component system of different surfactants and background electrolytes. In a recent work Kralchevsky *et al.* (1999) proposed a thermodynamic description of such liquids and interfaces, in which the effect of counterion binding on the surface tension and surface potential of ionic surfactant solutions was explicitly accounted for. In this work we present a solution of the drainage problem of a partially mobile thin liquid film between two bubbles when the continuous liquid phase is a complex mixture of ionic and nonionic surfactants and indifferent background electrolytes.
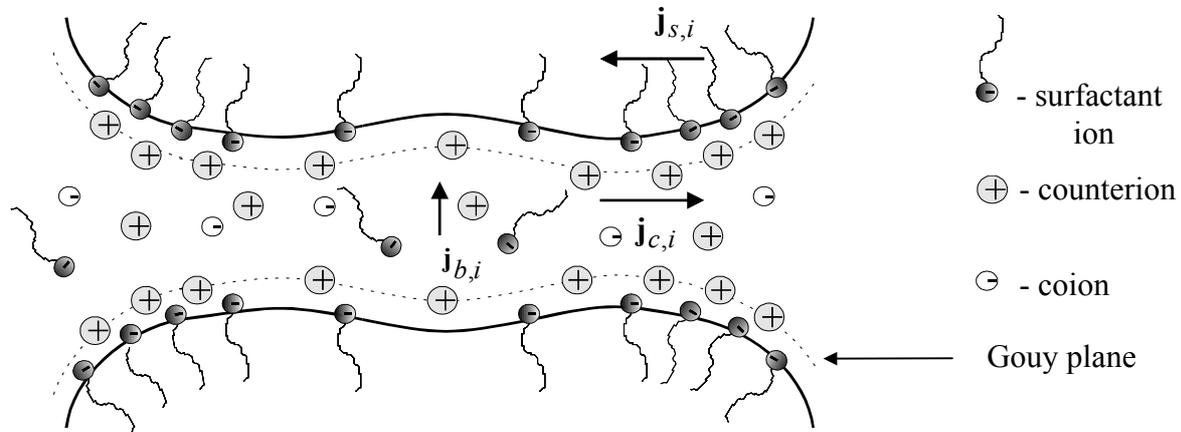
2. PHYSICAL BACKGROUND

Figure 1. Sketch of the film zone stabilized by an ionic surfactant solution containing dissolved non-amphiphilic electrolyte (salt). The distance between the Stern layer and the Gouy plane is exaggerated.

We consider a thin viscous liquid layer between two gas bubbles, which flows out due to their approach under the action of the external force, F (see Fig. 1). When surfactants are present in the solution, the liquid flow towards the meniscus carries away the surfactant molecules. The surface convective flux, $\mathbf{j}_{c,i}$, of each component ($i = 1,...,n$) generates reverse fluxes, which tend to restore the equilibrium distribution ($\mathbf{j}_{s,i}$ is the surface diffusion flux and $\mathbf{j}_{b,i}$ represents the bulk diffusion flux in Fig. 1). The process of adsorption of the ionic surfactants on the film interfaces is accompanied with an increase of the surface electric potential, ψ_s, and the charge density, ρ_s. In its own turn, the presence of surface electric potential is related to the formation of an electric double layer (EDL) inside the film. The charged surfaces repel the new-coming surfactant molecules (Fig. 1), which results in a 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 EDL. In the zone where the EDL of the two film interfaces overlap, the electric potential distribution changes, and it influences the diffusion processes in the gap region.

The non-uniform 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 its motion, which produce surface viscous stresses. Finally, the surface elements are under the action of the bulk stress caused by the liquid flow and electric potential distribution in the film. In the gap region for small film thickness the intermolecular forces 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, in a given moment, t, (quasi-steady-state assumption is used—all parameters depend implicitly on time through the local film thickness, H).

3. MATHEMATICAL MODEL

The problem for the drainage of symmetric films is described in a cylindrical coordinate system, Orz, where the bubble interface, S, is defined as $z = H(t,r)/2$, the middle plane is $z = 0$, and $\mathbf{n}$ is the unit normal at the surface S. In the literature (Ivanov, 1980; Ivanov & Dimitrov, 1988; Danov et al., 1999) the lubrication approximation is used for solution of the governing equations. The general frame for this approximation is imposed by: small Reynolds and Peclet numbers, small film thickness compared to the characteristic bubble radius, and small slope of the interfaces. The mass, momentum and force balance equations are applied to solve the problem.

3.1 Integrated mass balance and Poisson equations

In the lubrication approximation the leading order of the concentration in the bulk phase, c_i, obeys the local Poisson-Boltzmann distribution

$$c_i = c_{m,i} \exp\left[-\frac{q_i}{kT}(\psi - \psi_m)\right] \equiv c_{r,i} \exp\left(-\frac{q_i\psi}{kT}\right) , \quad (i = 1, ..., n), \quad (1)$$

where ψ and $\psi_m(t,r)$ are the electric potential in the bulk and in the middle of the film, k is the Boltzmann constant, and q_i, $c_{m,i}(t,r)$ and $c_{r,i}(t,r)$ are respectively the charge, the concentration in the middle plane, and the concentration in the thermodynamic reference phase (where $\psi \to 0$).

Using the bulk and surface mass balance equations for each component in the case of small Peclet numbers and lubrication approximation the final form of the conservation of mass equations is obtained:

$$\frac{\partial}{\partial t}\left(\Gamma_i + \int_0^{H/2} c_i dz\right) = -\frac{1}{r}\frac{\partial}{\partial r}\left\{r\left[\Gamma_i u + j_{s,i} + \int_0^{H/2}\left(c_i v_r + j_{b,i}\right)dz\right]\right\} , \quad (i = 1, ..., n). \quad (2)$$

Equation (2) expresses the fact that the change of the total mass across the film is compensated by the bulk and surface convection and diffusion fluxes (see Fig. 1). In Eq. (2) u is the fluid velocity at the surface, $\mathbf{v} = (v_r, v_z)$ is the bulk liquid velocity and Γ_i is the adsorption of surfactant ions on the film surfaces or the adsorption of counterions belonging to the Stern layer. Usually (Kralchevsky et al., 1999) the coions do not adsorb in the Stern layer and their adsorptions are practically equal to zero.

Using Eq. (1) the bulk diffusion flux, $j_{b,i}$, in Eq. (2) can be expressed by the relationship

$$j_{b,i} = -D_{b,i}\left(\frac{\partial c_i}{\partial r} + \frac{q_i c_i}{kT}\frac{\partial \psi}{\partial r}\right) = -D_{b,i}\frac{\partial c_{r,i}}{\partial r}\exp\left(-\frac{q_i \psi}{kT}\right) \ , \quad (i = 1, ..., n), \qquad (3)$$

where $D_{b,i}$ is the bulk diffusion coefficient and the second term in the left hand side of Eq. (3) (the so called "electromigration" term) accounts for the effect of the electric field on the surfactant diffusion. In order to define the surface diffusion fluxes we have to specify the mechanism of adsorption. It was proven in the literature (Ivanov & Dimitrov, 1988) that the diffusion-controlled adsorption is more important than the barrier controlled adsorption for film thinning. From a thermodynamic viewpoint this means that the total electro-chemical surface potential of each species, $\mu_{s,i}$, is equal to the electro-chemical bulk potential in the contiguous layer (Kralchevsky *et al.*, 1999). Hence, from Eq. (1) the total surface diffusion flux can be written in the form

$$j_{s,i} = -\frac{D_{s,i}\Gamma_i}{kT}\frac{\partial \mu_{s,i}}{\partial r} = -\frac{D_{s,i}\Gamma_i}{c_{r,i}}\frac{\partial c_{r,i}}{\partial r} \ , \quad (i = 1, ..., n), \qquad (4)$$

where $D_{s,i}$ is the surface diffusion coefficient.

The electric potential, ψ, is related to the bulk charge density through the known Poisson equation, which has the following first integral in the case of lubrication approximation

$$\left(\frac{\partial \psi}{\partial z}\right)^2 = \frac{8\pi kT}{\varepsilon}\sum_{i=1}^{n}c_{r,i}\left[\exp\left(-\frac{q_i \psi}{kT}\right) - \exp\left(-\frac{q_i \psi_m}{kT}\right)\right], \qquad (5)$$

where ε is the dielectric permittivity. The condition for electro-neutrality of the solution as a whole is equivalent to the Gauss law written for the surface charge density, $\rho_{s,e}$. In the lubrication approximation it reads:

$$\frac{\partial \psi}{\partial z} = \frac{4\pi}{\varepsilon}\sum_{i=1}^{n}q_i \Gamma_i \equiv \frac{4\pi}{\varepsilon}\rho_{s,e} \qquad \text{at } z = H/2 . \qquad (6)$$

The assumption for diffusion-controlled adsorption allows us to close the system of equations (1)-(6) with the respective isotherms for the different species: $\Gamma_i = \Gamma_i\left(c_{1,s}, c_{2,s}, ..., c_{n,s}\right)$. The list of commonly encountered isotherms is given in a recent work (Kralchevsky *et al.*, 1999). Therefore, if we know the velocity distribution, the problem for the concentrations, adsorptions and electrical potential distributions is completed.

3.2 Integrated bulk continuity and tangential stress balance equations

In the case of a multi-component ionic liquid mixture the density of the electric force, $\rho_{b,e}\mathbf{E}$ ($\rho_{b,e}$ is the bulk charge density and $\mathbf{E}=-\nabla\psi$ is the electric field), plays the role of a spatial body force in the known Navier-Stokes equation of motion. For low Reynolds numbers and small film thickness, the pressure in the continuous phase, p, depends only on the radial coordinate, r, time, t, and the electric field (osmotic part of the pressure):

$$p = p_m + kT\sum_{i=1}^{n}\left(c_i - c_{m,i}\right) \equiv p_r + kT\sum_{i=1}^{n}c_i \; , \tag{7}$$

where $p_m(t,r)$ and $p_r(t,r)$ are respectively the pressures in the middle of the film and in the thermodynamic reference phase (where $\psi\to 0$). The substitution of Eqs (1) and (7) into the radial component of the momentum balance equation leads to the following expression for the radial component of the velocity in the framework of lubrication approximation

$$\eta\frac{\partial^2 v_r}{\partial z^2} = \frac{\partial p_r}{\partial r} + kT\sum_{i=1}^{n}\frac{\partial c_{r,i}}{\partial r}\exp\left(-\frac{q_i\psi}{kT}\right) \; , \tag{8}$$

The dynamic viscosity is denoted by η in Eq. (8). The electric force in Eq. (8) is a complex function of z. In order to simplify all equations bellow we introduce the new function, f_i, which is the solution of the following boundary problem:

$$\frac{\partial^3 f_i}{\partial z^3} = \exp\left(-\frac{q_i\psi}{kT}\right) \; ; \quad f_i = 0 \; \text{ and } \; \frac{\partial^2 f_i}{\partial z^2} = 0 \; \text{ at } z=0; \quad \frac{\partial f_i}{\partial z} = 0 \; \text{ at } z = H/2. \tag{9}$$

Hence, using Eqs. (8) and (9), the symmetry of the film and the kinematic boundary condition at the film surface, one can calculate the distribution of the radial component of the velocity

$$v_r = u + \frac{1}{2\eta}\frac{\partial p_r}{\partial r}\left(z^2 - \frac{H^2}{4}\right) + \frac{kT}{\eta}\sum_{i=1}^{n}\frac{\partial c_{r,i}}{\partial r}\frac{\partial f_i}{\partial z} \; . \tag{10}$$

The boundary condition for the balance of the surface excess linear momentum takes into account the influence of the surface tension gradient (capillary and Marangoni effects), the surface viscosity (Boussinesq effect), and the influence of the electric part in the bulk pressure stress tensor (see Kralchevsky *et al.*, 1999). In lubrication approximation the tangential stress boundary condition at the interface, utilizing Eqs. (6) and (10), is simplified to

$$\frac{H}{2}\frac{\partial p_r}{\partial r} + kT\sum_{i=1}^{n}f_{s,i}''\frac{\partial c_{r,i}}{\partial r} + \rho_{s,e}\frac{\partial\psi}{\partial r} + \frac{2\pi}{\varepsilon}\rho_{s,e}^2\frac{\partial H}{\partial r} = \frac{\partial\sigma}{\partial r} + \eta_s\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(ru)\right]. \tag{11}$$

In Eq. (11) $\eta_s = \eta_{sh} + \eta_{dil}$ is the total surface viscosity, defined as a sum of the interfacial shear, η_{sh}, and dilatational, η_{dil}, viscosities, and $f''_{s,i}$ is the value of $\partial^2 f_i / \partial z^2$ at $z = H/2$.

From the bulk continuity equation ($\nabla \cdot \mathbf{v} = 0$) and the kinematic boundary condition the integrated bulk continuity equation can be written in the following form:

$$\frac{\partial H}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(2r \int_0^{H/2} v_r dz \right) = 0 . \tag{12}$$

When the surface equation of state (dependence of the interfacial tension, σ, on the adsorption, for example see Kralchevsky *et al.*, 1999) and the film profile, H, are known, then Eqs. (10)-(12) give the velocity, v_r, the surface velocity, u, and the pressure, p_r, distributions.

3.3 Drainage velocity and force balance

In the general case (Yantsios & Davis, 1990, 1991) the local velocity of surface approach depends on the radial coordinate through the normal stress boundary condition. Then Eq. (12) is a stiff nonlinear differential equation, which is difficult to be solved numerically. The quasi-steady state assumption is used in most of the publications in the literature to avoid this problem—all variables depend implicitly on time through the local film thickness. Therefore, the local velocity of surface approach does not depend on the radial coordinate and it is equal to the so-called drainage velocity, $V = -\partial H / \partial t$. If we substitute Eq. (10) into Eq. (12) and integrate the obtained result, the drainage velocity can be calculated as

$$V = \frac{2}{r}\left(Hu - \frac{H^3}{12\eta}\frac{\partial p_r}{\partial r} + 2\frac{kT}{\eta}\sum_{i=1}^{n} f_{s,i}\frac{\partial c_{r,i}}{\partial r} \right) , \tag{13}$$

where $f_{s,i}$ is the value of f_i at $z = H/2$.

The film between the bubbles thins due to the action of the external force, F, which in the quasi-steady state approach is balanced by the hydrodynamic drag force and intermolecular forces. Hence, in the lubrication approximation we obtain

$$F = 2\pi \int_0^\infty \left(p_m + \Pi_{vw} - p_\infty \right) r dr \equiv 2\pi \int_0^\infty \left(p_r + kT\sum_{i=1}^{n} c_{m,i} + \Pi_{vw} - p_\infty \right) r dr . \tag{14}$$

p_∞ in Eq. (14) is the pressure at infinity in the meniscus region. Knowing the film profile and the type of intermolecular interactions (van der Waals, steric, etc. disjoining pressure, except the electrostatic disjoining pressure component), the external force can be connected with the hydrodynamic drag force, F_{hd}, acting on the bubbles. It is important to note that the electrostatic component of the disjoining pressure is already included in the osmotic term of the pressure in the middle of the film.

The disjoining pressure isotherm, $\Pi(H)$, for symmetric foam film stabilized by SDS is plotted in Fig. 2. The Frumkin adsorption isotherm is used for calculation of the thermodynamic equation of state and the relationships between subsurface and surface concentrations of surface-active ions and counterions, respectively. The adsorption

coefficients are taken from Kralchevsky *et al.* (1999). When the draining film reaches the thickness at which the disjoining pressure equals the capillary pressure, the external force alters to zero. Then the film reaches its thermodynamic stable equilibrium state and the drainage process stops. Due to some thermal or mechanical fluctuations this equilibrium may become unstable and the film may rupture or black spots may form. This problem is discussed in the other paper presented on the conference (Effect of Ionic Surfactants on the Stability of Plane-Parallel Film). The present study discusses the drainage process up to the equilibrium point (Fig. 2).
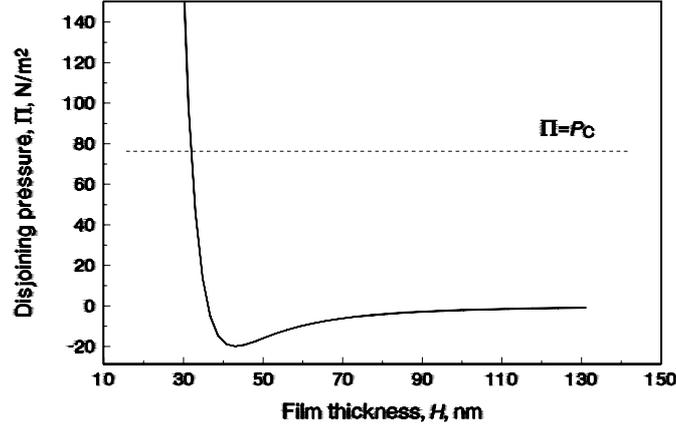

Figure 2. Sketch of disjoining pressure isotherm, Π vs. H

4. DRAINAGE VELOCITY OF PLANE-PARALLEL FILMS AT SMALL DEVIATIONS FROM EQUILIBRIUM

The problem (1)-(14) has no analytical solution, due to the strong nonlinear dependence of the surface tension and adsorption on the subsurface concentration. In the literature (Ivanov, 1980; Ivanov & Dimitrov, 1988; Danov *et al.*, 1999) the following assumption is used: small deviations from equilibrium

$$\Gamma_i = \Gamma_{e,i} + \delta\Gamma_i \ , \qquad c_i = c_{e,i} + \delta c_i \ , \qquad c_{r,i} = c_{\infty,i} + \delta c_{r,i} \ , \qquad \psi = \psi_e + \delta\psi \ , \quad (15)$$

where the subscript "e" denotes the quasi-equilibrium values of the corresponding parameters (at which the velocity is zero); with δ we denote small deviations from the basic state of the parameters; $c_{\infty,i}$ is the concentration of the i-th ion at infinity in the meniscus region. The quasi-equilibrium distributions of the concentrations, adsorption and electric potential are described by equations (1), (5), (6) and the respective isotherms. The experimental results (Ivanov & Dimitrov, 1988) showed that the complete process of drainage of a thin liquid film has five stages, depending on the hydrodynamic and intermolecular interactions. However, the time limiting factors for coalescence or flocculation are the approach of drops as non-deformed spheres (earliest stage), and the drainage of the formed almost plane-parallel film between the drops or bubbles. We will discuss below the latest stage of the bubbles approach—the plane-parallel film thinning. In the case of symmetric electrolytes and plane-parallel films the exact analytical formulas are given in Kralchevsky *et al.* (1997).

If we substitute the series (15) into the mass balance equations (2)-(4) using the velocity profile (10) and integrating the result, a simple relationship for the gradient of perturbations in the concentration in the reference phase can be derived:

$$\frac{\partial \delta c_{r,i}}{\partial r} = \alpha_i u + \beta_i \frac{\partial p_r}{\partial r} \ , \qquad \gamma_i \equiv \frac{D_{s,i} \Gamma_{e,i}}{c_{\infty,i}} + D_{b,i} f''_{s,i},$$

(16.a)

$$\alpha_i \equiv \left[\Gamma_{e,i} + c_{\infty,i} \left(f''_{s,i} - \frac{H}{2} f'''_{s,i} \right) \right] / \gamma_i \ , \qquad \beta_i \equiv \frac{c_{\infty,i}}{\eta \gamma_i} \left(f_{s,i} + \frac{H^3}{24} f'''_{s,i} \right) .$$

(16.b)

All coefficients α_i, β_i, and γ_i ($i = 1,...,n$) in Eq. (16) are known parameters. They are calculated from the basic (quasi-equilibrium) state. The functions f_i and their derivatives are defined through the equilibrium distribution of the electric potential.

The surface velocity is a linear function of the radial coordinate in the case of plane-parallel film and it follows from Eq. (11) that the surface viscosity cannot influence the mobility of the interface (see Ivanov & Dimitrov, 1988). We proved that the effect of the deviation of the surface electric potential is also negligible. That is why the tangential stress balance equation (11) is simplified to

$$\frac{H}{2} \frac{\partial p_r}{\partial r} = \sum_{i=1}^{n} f'''_{s,i} \left(\frac{\partial \sigma}{\partial c_{s,i}} \right)_e \frac{\partial \delta c_{r,i}}{\partial r} .$$

(17)

In Eq. (17) the derivative of the surface tension is calculated from the respective equation of state and isotherms at equilibrium. After the substitution of Eq. (16) into Eq. (17) the final form of the surface velocity is derived

$$u = \frac{H^2}{12 \varepsilon_f \eta} \frac{\partial p_r}{\partial r} \ , \qquad \varepsilon_f^{-1} \equiv \frac{6\eta}{H^2} \left[H - 2 \sum_{i=1}^{n} \beta_i f'''_{s,i} \left(\frac{\partial \sigma}{\partial c_{s,i}} \right)_e \right] / \sum_{i=1}^{n} \alpha_i f'''_{s,i} \left(\frac{\partial \sigma}{\partial c_{s,i}} \right)_e .$$

(18)

It is seen that the mobility of the interface depends on the parameter ε_f. In the particular case of one component nonionic surfactant solution the known formula for the so called in the literature foam parameter, ε_f, can be obtained from Eqs. (9), (16), (18)

$$\frac{1}{\varepsilon_f} = b + \frac{h_s}{H} \ , \qquad b \equiv \frac{3\eta D_b}{E_G} \left(\frac{\partial c}{\partial \Gamma} \right)_e \ , \qquad h_s \equiv \frac{6\eta D_s}{E_G} ,$$

(19)

where the Gibbs elasticity of the adsorption layer is $E_G \equiv -\left(\partial \sigma / \partial \ln \Gamma \right)_e$. After the substitution of Eq. (18) into Eq. (13) the pressure gradient as a function of the material properties of the interfaces and the drainage velocity is derived to be

$$\frac{\partial p_r}{\partial r} = -\frac{\varepsilon_f}{1 + \varepsilon_f} \frac{6\eta r V}{H^3} .$$

(20)

Then from Eq. (14) the final form of the hydrodynamic drag force becomes

$$F_{hd} \equiv F - \pi R^2 \left(\Pi_{vw} + \Pi_{el} \right) = \frac{3\pi \eta V R^4}{2 H^3} \frac{\varepsilon_f}{1 + \varepsilon_f} ,$$ (21)

where R is the radius of the plane-parallel film and the electrostatic component of the disjoining pressure for small deviation from quasi-equilibrium is given as in the classical Langmuir form: $\Pi_{el} = kT \sum_{i=1}^{n} c_{\infty,i} \exp\left[- q_i \psi_m / (kT) \right]$. Therefore, the electrostatic interaction decelerates the drainage of the film and depending on the surfactant and background electrolyte concentrations it can become so large to stop the film drainage ($\mathbf{v} = \mathbf{0}$), i.e. the equilibrium film thickness can be reached (see Fig. 2).

The process of film drainage depends also on the foam parameter, which takes into account the mobility of interfaces. The dependence of the inverse foam parameter, ε_f^{-1}, on the surfactant concentration, $c_{1,\infty}$, is shown in Fig.3. The computations are made for foam film stabilized by SDS (without salt) with the following physical parameters: diffusion coefficients, $D_{1,b} = D_{1,s} = 5.5 \times 10^{-10} \text{ m}^2 / \text{s}$ and $D_{2,b} = D_{2,s} = 6.06 \times 10^{-10} \text{ m}^2 / \text{s}$, and viscosity, $\eta = 0.82 \times 10^{-3} \text{ Ns} / \text{m}$. The Gibbs elasticity is very high for large surfactant concentration. Therefore, the foam parameter is a large parameter and the interface is tangentially immobile. Lower surfactant concentration and faster diffusion processes lead to higher mobility of the interface. The foam parameter, defined through Eq. (18) depends on the film thickness and, as it is seen from Fig. 3, the mobility of the interfaces increases for thinner films. For every film thickness, at high surfactant concentrations the inverse foam parameter tends to the bulk diffusion parameter, b, because the interfaces become tangentially immobile and the surface diffusion is negligible.
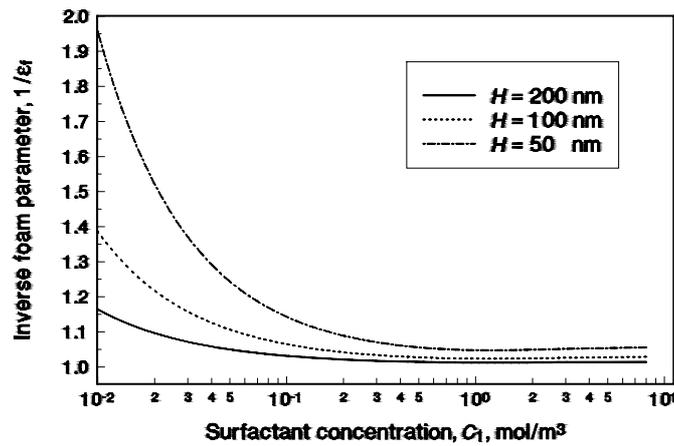

Figure 3. Inverse foam parameter vs. surfactant concentration

From physical viewpoint the main conclusion in the case of small deviations and plane-parallel films is that the electric potential affects the film thinning in two ways: (i) by slowing down the diffusion of the surface active ions and by accelerating the diffusion of coins (these

affect the mobility of the interface in a very complex way); (ii) by increasing the disjoining pressure trough the electrostatic repulsion term (the classical Langmuir approach).

5. CONCLUSIONS

A theoretical model for calculation of the influence of surfactants and background electrolytes on the approaching velocity of two bubbles is developed. It takes into account the effects of the surface viscosity, the electric and surfactant components of the surface elasticity, and the surface and bulk diffusion processes. The surfactant ions, coions and counterions distributions in the film phase obey the quasi-Poisson-Boltzmann distributions. The time-limiting adsorption processes are shown to be diffusion controlled. The overlapping of the EDL produces an additional electrostatic repulsion, which stabilizes the film and decelerates the process of film drainage. The model gives a complex system of equations which can be solved numerically for a given film profile.

In the case of plane-parallel films and small deviation from quasi-equilibrium state (basic state when the velocity is zero) the exact analytical solution of the problem is derived. It presents a simple relation between the external force, film radius and thickness, and the foam parameter. It is shown that the bulk distribution of the ions affects the drainage process through the classical electrostatic disjoining pressure and the change of the surface mobility of the film.

There have been numerous attempts to formulate simple rules connecting the foam and emulsion stability with the surfactants properties: the Bancroft rule; Griffin's criterion, which introduces the concepts of the hydrophilic-hydrophobic balance (HLB); the phase inversion temperature (PIT) rule of Schinoda and Friberg; etc. Ivanov (1980) and Kralchevsky *et al.* (1997) gave a new interpretation of the Bancroft rule, taking into account the dynamic processes in the film between two colliding emulsion droplets. The obtained results can be applied in order to generalize this criterion for solutions containing various ions.

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