

## EFFECT OF IONIC SURFACTANTS ON THE STABILITY OF PLANE-PARALLEL FILMS

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***Abstract.** The stability of a partially mobile thin liquid plane-parallel film between two gas or oil phases is studied. The long wave approximation is used to analyze the influence of soluble ionic surfactants and non-surface active background electrolyte on the increment/decrement of fluctuations. The material properties of the corresponding multiphase flow and interfaces are taken into account. The equilibrium state of the film is described by the classical DLVO theory in which the Van der Waals and electrostatic disjoining pressures are included. The fluctuation analysis of the electro-diffusion fluxes, velocity of the components, concentrations, electric potential and film thickness give the analytical criteria for stability of the equilibrium state. Numerical results show changes of the stability region with increasing surfactant concentration and significant influence of the background electrolyte. The stabilizing effects of the Gibbs elasticity, surface and bulk viscosities are demonstrated.. The results are useful for control of the foam breakdown in the industrial systems.*

***Keywords:** Ionic surfactant solution, Background electrolyte, Thin liquid film stability, Critical thickness, Gibbs elasticity*

### 1. INTRODUCTION

The stability of thin liquid films is an important problem in diverse areas of science and technology. Technological and biological examples include foam and emulsion stability (Kralchevsky *et al.*, 1997); displacement of crude oil by gas and foam from rock pores (Ramamohan and Slattery, 1984); safety of light water cooled nuclear power plants (Lienhard *et al.*, 1978); the rupture of the tear film in the human eye (Lin and Brenner, 1982); etc. This paper examines the stability of thin liquid film occurring between two drops or bubbles in a dispersion stabilized by ionic surfactants in the presence of a background electrolyte (inorganic salt).

The thin liquid film rupture is due to thermal fluctuations which lead to corrugations of the film surfaces. These corrugations give rise to two forces: (i) capillary pressure, which tends to resist any deformation on the surface, and (ii) disjoining pressure, which can amplify the

amplitude of the corrugations. Therefore, there exists a transition thickness at which the characteristics of the waves change. For thicknesses smaller than the transitional one the film is unstable and, as the amplitude of the wave increases, it ruptures.

The problem of film stability has been investigated by many authors. Early studies attributed the film rupture to the onset of a thermodynamically unstable state during the drainage process and the usual approach was to calculate the free energy of the film as a function of its thickness (Frenkel, 1955). De Vries (1958) was the first to supplement the thermodynamic studies of film stability with a kinetic treatment of the mechanism of rupture. Further investigations revealed the importance of the interfacial tension, van der Waals and electrostatic forces, density, viscosity ratio of the two phases and interfacial elasticity for determining the film stability (see the review of Maldarelli and Jain, 1988). It was found that for a thin film between identical phases there exist two modes of vibration of the film: symmetric and antisymmetric. The symmetric long waves were shown to be responsible for the film rupture. Ivanov *et al.* (1974) analyzed the stability of films containing low concentrations of surface active species. Those authors included the effects of surface diffusion and surface viscosity and demonstrated that the decrease in the critical thickness with increasing surfactant concentration is due to surface viscosity.

Most of the publications in the literature (see the review of Danov *et al.*, 1999) describe the stability of plane-parallel films in the case of nonionic surfactants. In various applications the bulk phase is a multi-component system of different kind of surfactants and background electrolytes. The thermodynamics of such liquids and interfaces is studied by Kralchevsky *et al.* (1999). In this work we present a solution of the stability problem of an equilibrium plane-parallel thin liquid film between two bubbles when the continuous liquid phase is a complex mixture of ionic and nonionic surfactants and background electrolytes.

## 2. PHYSICAL BACKGROUND

The stability of foams and emulsions depends on the stability of the thin liquid films formed between the colliding particles. In the classical concept of dispersion stability, the so called DLVO theory (see the review of Kralchevsky *et al.*, 1997), the total interaction between particles is supposed to be a superposition of van der Waals and electric double layer interactions. The total disjoining pressure,  $\Pi$ , and the particle-particle interaction energy,  $U$ , are presented in the form:  $\Pi = \Pi_{vw} + \Pi_{el}$ ;  $U = U_{vw} + U_{el}$ .  $\Pi_{vw}$  is the van der Waals attractive disjoining pressure, which leads to fast drainage and rupture of the films, and  $\Pi_{el}$  is the electric repulsive disjoining pressure, which may counterbalance the van der Waals attraction and stabilize the films. A typical disjoining pressure isotherm,  $\Pi(H)$ , is depicted in Fig. 1a. The maximum represents a barrier against coagulation, the primary minimum appears if strong short-range repulsive forces (steric forces) present, and the secondary minimum is usually small, but for larger drops could be deep enough to cause coagulation.

Thermodynamic equilibrium condition is reached when the total disjoining pressure,  $\Pi$ , equals the capillary pressure,  $P_c$ :  $\Pi = P_c$ . This equilibrium condition can be satisfied at the three points shown in Fig. 1a. Point 1 corresponds to a film, which is stabilized by double-layer repulsion. Point 3 corresponds to unstable equilibrium and cannot be observed experimentally. Point 2 corresponds to a very thin film, which is stabilized by short-range repulsion (Newton black film).

It is known from experiments that for low surfactant concentrations the equilibrium state 1 (Fig. 1a) is thermodynamically stable, but at high surfactant concentrations the mechanical equilibrium in point 1 is unstable—the film ruptures, or Newton black film is formed. This

instability may be a result of thermal or mechanical fluctuations in the film shape (Fig. 1b), which disturb the surfactant adsorption, concentration and surface potential. Then regions with lower subsurface concentration and adsorption appear. In these areas the surface charge density decreases and the van der Waals attraction prevails over the electrostatic repulsion. Depending on the dissipation of wave energy due to the surface elasticity and viscosity, the equilibrium may become unstable. The rupture can be prevented also by bulk and surface diffusion fluxes, which tend to restore the equilibrium.

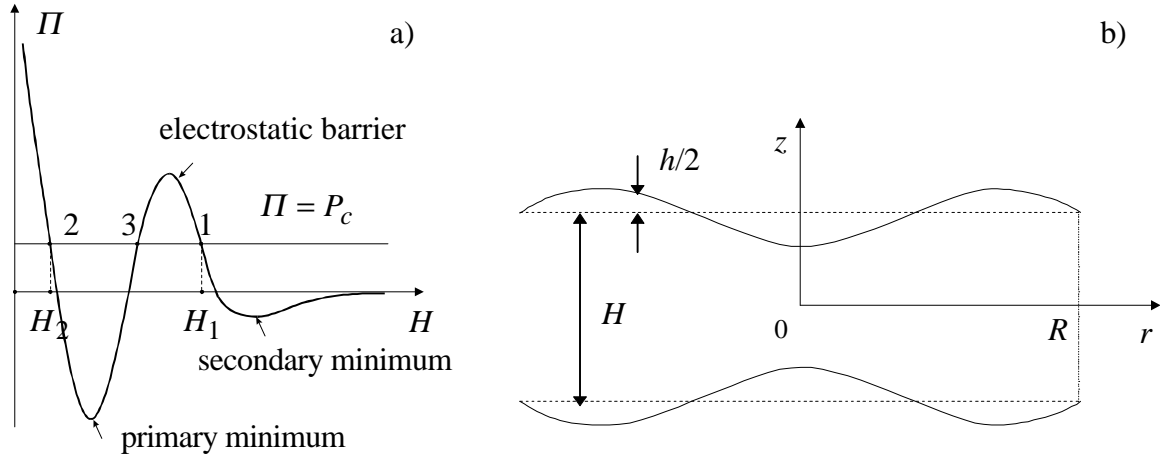


Figure 1 - Physical illustration of the system under consideration: a) a typical disjoining pressure isotherm,  $\Pi$  vs.  $H$ ; b) fluctuation waves at film surfaces.

### 3. MATHEMATICAL MODEL

The problem for the stability of a plane-parallel, non-draining film, formed between two drops or bubbles (Fig. 1b), is described in a cylindrical coordinate system,  $Orz$ , where the bubble interface,  $S$ , is defined as  $z = (H+h)/2$  and the middle plane is  $z = 0$ . In the literature (Maldarelli and Jain, 1988) the long wave approximation is used for solution of the governing equations. The general frame of this approximation is represented by the following assumptions: small film thickness compared to the characteristic bubble radius; the wavelength is of the order of the film radius,  $R$ ; the fluctuation in the film thickness,  $h$ , is much smaller than the wavelength and the film thickness. In order to solve the problem, a linear stability analysis can be applied.

#### 3.1 Equilibrium state

In the equilibrium state the velocity in the film is zero ( $\mathbf{v} = 0$ ). The equilibrium distributions of the ion concentrations in the bulk phase,  $c_i$ , obey the Boltzmann law

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

where  $\psi(z)$  and  $\psi_m$  are the electric potentials in the bulk phase and in the middle of the film,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $q_i$ ,  $c_{m,i}$  and  $c_{\infty,i}$  are the charge, the concentration in the middle plane, and the initial concentration of the ions in the solution, respectively.

The electric potential,  $\psi$ , is related to the bulk charge density through the known Poisson equation. In the case of equilibrium [Eq. (1)], for symmetric films, the following first integral holds:

$$\left(\frac{d\psi}{dz}\right)^2 = \frac{8\pi kT}{\varepsilon} \sum_{i=1}^n c_{\infty,i} \left[ \exp\left(-\frac{q_i\psi}{kT}\right) - \exp\left(-\frac{q_i\psi_m}{kT}\right) \right], \quad (2)$$

where  $\varepsilon$  is the dielectric permittivity. The electro-neutrality condition for the solution as a whole is equivalent to the Gauss law written for the surface charge density,  $\rho_{s,e}$ . At the equilibrium thickness,  $H$ , it follows:

$$\frac{d\psi}{dz} = \frac{4\pi}{\varepsilon} \sum_{i=1}^n q_i \Gamma_i \equiv \frac{4\pi}{\varepsilon} \rho_{s,e} \quad \text{at } z = H/2. \quad (3)$$

In Eq. (3)  $\Gamma_i$  are the adsorptions of the surface active ions at the interface, and of the counterions or coions in the Stern layer.

In the classical DLVO theory the equilibrium condition is reached when the total disjoining pressure is equal to the capillary pressure (see Fig. 1a). Here we will investigate the stability of the first equilibrium thickness, where the steric interactions are negligible and

$$-\frac{A_H}{6\pi H^3} + kT \sum_{i=1}^n (c_{m,i} - c_{\infty,i}) = \frac{2\sigma}{R_c}, \quad (4)$$

where  $A_H$  is the Hamaker constant,  $\sigma$  is the interfacial tension, and  $R_c$  is the bubble or drop radius. The first term in Eq. (4) is the van der Waals disjoining pressure and the second one represents the electrostatic disjoining pressure which is equal to the osmotic pressure built from the electric double layer (EDL) overlapping [the Langmuir formula for the electrostatic disjoining pressure, see Kralchevsky *et al.* (1997)].

To close the system of equations (1)-(4) the respective isotherms for each species,  $\Gamma_i = \Gamma_i(c_{s,1}, c_{s,2}, \dots, c_{s,n})$ , are used. The subscript ‘‘s’’ denotes the value of the parameter in the contiguous film phase. The list of corresponding isotherms is given in a recent work (Kralchevsky *et al.*, 1999). Therefore, for any given kind of surfactants and added salts from Eqs. (1)-(4) and respective isotherms we can calculate all parameters of the equilibrium state.

The dependence of the equilibrium film thickness,  $H$ , and the corresponding electric potentials in the middle plane,  $\psi_m$ , and at the surface,  $\psi_s$ , on the initial surfactant ion concentration,  $c_{\infty,1}$ , are plotted in Figs. 2a and 2b. Numerical results are computed for dispersion system stabilized by sodium dodecyl sulfate (SDS) in the presence of different amount of salt (NaCl). Both the surfactant and salt are symmetric (1:1) electrolytes. The calculations are made by using the Frumkin adsorption isotherm and surface tension isotherm which is appropriate for air-water interfaces. The values of the adsorption parameters are taken from Kralchevsky *et al.* (1999). It is seen that the equilibrium film thickness,  $H$ , and the electric potential in the middle plane,  $\psi_m$ , decrease with increasing surfactant concentration,  $c_{\infty,1}$ . The surface electric potential,  $\psi_s$ , has a maximum which corresponds to the maximum adsorption of the surface active ions on the surface. Addition of more surfactant results in

increasing counterion adsorption while the adsorption of the active ions remains constant. The surface charge decreases which leads to decreasing surface electric potential. Adding salt reduces the thickness of EDL and causes the electric potentials in the middle plane and on the surface to decrease (Fig. 2b). The van der Waals attractive force does not depend on the surfactant concentration. The background electrolyte decreases the electrostatic repulsion and the equilibrium takes place at smaller thickness (Fig. 2a).

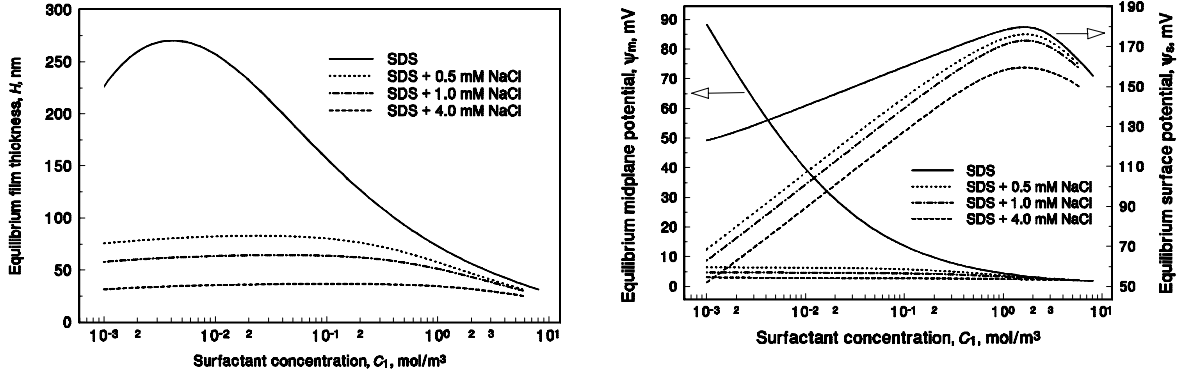


Figure 2 - Dependence of the equilibrium parameters on the surfactant concentration: a) film thickness,  $H$ ; b) electric potentials  $\psi_m$  and  $\psi_s$ .  $R_c = 2$  mm and  $A_H = 4 \times 10^{-20}$  J.

### 3.2 Equations of motion and integrated mass balance for fluctuations

Since the film is thin and the wavelength is of the order of the film radius, the liquid motion can be described by simplified Navier-Stokes equations. For displacements having azimuthal symmetry, the dynamic equations for the disturbances are

$$\eta \frac{\partial^2 v_r}{\partial z^2} = \frac{\partial p^f}{\partial r} + kT \sum_{i=1}^n c_i q_i \frac{\partial \psi^f}{\partial r}, \quad (5.a)$$

$$\frac{\partial p^f}{\partial z} + \sum_i c_i q_i \frac{\partial \psi^f}{\partial z} + \sum_i c_i^f q_i \frac{\partial \psi}{\partial z} = 0, \quad (5.b)$$

In equations (5)  $\eta$  is the dynamic viscosity,  $p^f$  is the fluctuation in the dynamic pressure, and  $v_r$  and  $v_z$  are the radial and axial components of the velocity generated by surface waves. The superscript "f" denotes the fluctuations of the respective equilibrium parameters (bulk concentrations, pressure and electric potential). From the continuity equation,  $\nabla \cdot \mathbf{v} = 0$ , and the Poisson equation it follows that the fluctuation in the pressure,  $p^f$ , depends only on the radial coordinate,  $r$ , time,  $t$ , and electric field (osmotic part of the pressure):

$$p^f = p_m^f + \frac{\varepsilon}{4\pi} \frac{d\psi}{dz} \frac{\partial \psi^f}{\partial z} \equiv p_r^f + kT \sum_{i=1}^n c_i^f, \quad (6)$$

where  $p_m^f(t, r)$  and  $p_r^f(t, r)$  are the pressure fluctuations in the middle of the film and in the thermodynamic reference phase (where  $\psi \rightarrow 0$ ).

As we solve the stability problem at long wave limit the concentration in the bulk phase,  $c_i$ , obeys the Poisson-Boltzmann distribution. Hence, the fluctuations in concentrations caused by surface waves are presented as:

$$c_i \rightarrow c_i + c_i^f, \quad c_i^f = \left( c_{r,i}^f - \frac{q_i c_{\infty,i}}{kT} \psi^f \right) \exp\left( -\frac{q_i \psi}{kT} \right), (i = 1, \dots, n), \quad (7)$$

where  $c_{r,i}^f(r, t)$  are the fluctuations in concentrations in the thermodynamic reference phase.

In order to simplify all equations below we introduce a new function,  $f_i$ , which is the solution of the following boundary problem at equilibrium:

$$\frac{d^3 f_i}{dz^3} = \exp\left( -\frac{q_i \psi}{kT} \right); \quad f_i = 0 \quad \text{and} \quad \frac{d^2 f_i}{dz^2} = 0 \quad \text{at} \quad z = 0; \quad \frac{d f_i}{dz} = 0 \quad \text{at} \quad z = H/2. \quad (8)$$

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

$$\Gamma_i u + \int_0^{H/2} v_r (c_i - c_{i,s}) dz = \gamma_i \frac{\partial c_{r,i}^f}{\partial r}, \quad \gamma_i \equiv \frac{D_{s,i} \Gamma_i}{c_{\infty,i}} + D_{b,i} f_{s,i}'' , \quad (i = 1, \dots, n), \quad (9)$$

with respective bulk and surface diffusion coefficients,  $D_{b,i}$  and  $D_{s,i}$ , the fluid velocity at the surface,  $u$ , and  $f_{s,i}''$  denoting the value of  $d^2 f_i / dz^2$  at  $z = H/2$ . Equation (9) explains that the total convective flux of  $i$ -th species (the left hand side) is counterbalanced by the corresponding total bulk and surface diffusion fluxes (the right hand side). Usually (Kralchevsky *et al.*, 1999) the coions do not adsorb in the Stern layer.

### 3.3 Boundary conditions

We restrict our attention to symmetric disturbances. We assume that the surface displacements from the undisturbed state are small and thus the resulting disturbances ( $v_r, v_z, p^f$ ) may be assumed to be small too. With the above considerations, the linearized kinematic boundary conditions at the interface,  $z = H/2$ , become  $v_r = u$  and  $2v_z = \partial h / \partial t$ . The normal and tangential stress boundary conditions at  $z = H/2$  transform to

$$h \frac{d \Pi}{d H} + \frac{\sigma_a}{2} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) + p_m^f = 0, \quad (10.a)$$

$$\frac{H}{2} \frac{\partial p_r^f}{\partial r} + kT \sum_{i=1}^n f_{s,i}'' \frac{\partial c_{r,i}^f}{\partial r} + \rho_{s,e} \frac{\partial}{\partial r} \left( \psi^f + \frac{d \psi}{dz} \frac{h}{2} \right) = \frac{\partial}{\partial r} \left[ \sigma_a + \frac{\eta_s}{r} \frac{\partial}{\partial r} (ru) \right]. \quad (10.b)$$

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 are taken into account in the normal and tangential stress boundary conditions [Eq. (10)]. The following notations are used:  $\eta_s = \eta_{sh} + \eta_{dil}$  is the total surface viscosity, defined as a sum of the interfacial shear,  $\eta_{sh}$ , and dilatational,  $\eta_{dil}$ , viscosities; the derivative of the disjoining pressure,  $\Pi$ , at the equilibrium is  $d\Pi/dH$ , where the electric part of the disjoining pressure has to be included in  $\Pi$  (see Section 2);  $\sigma_a$  is the adsorption part of the interfacial tension (as it was shown by Kralchevsky *et al.* (1999) the total surface tension is a sum of the adsorption part and the term coming from the non-isotropy of the electric pressure tensor in the EDL).

From the bulk continuity equation and the kinematic boundary condition the integrated bulk continuity equation for fluctuations can be written in the following form:

$$\frac{\partial h}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( 2r \int_0^{H/2} v_r dz \right) = 0. \quad (11)$$

In order to complete the formulation of the problem, using Eqs. (5.a) and (8), the symmetry of the film and the kinematic boundary condition at the film surface, the distribution of the radial component of the fluctuation velocity is calculated to be

$$v_r = u + \frac{1}{2\eta} \frac{\partial p_r^f}{\partial r} \left( z^2 - \frac{H^2}{4} \right) + \frac{kT}{\eta} \sum_{i=1}^n \frac{\partial c_{r,i}^f}{\partial r} \frac{df_i}{dz}. \quad (12)$$

Substituting Eq. (12) into Eqs. (9) and (11), the mass balance and the continuity equation become:

$$u \left[ \Gamma_i + c_{\infty,i} \left( f_{s,i}'' - \frac{H}{2} f_{s,i}''' \right) \right] + \frac{c_{\infty,i}}{\eta} \frac{\partial p_r^f}{\partial r} \left( f_{s,i} + \frac{H^3}{24} f_{s,i}''' \right) = \gamma_i \frac{\partial c_{r,i}^f}{\partial r}, \quad (13)$$

$$\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( uH - \frac{H^3}{12\eta} \frac{\partial p_r^f}{\partial r} + \frac{2kT}{\eta} \sum_{i=1}^n f_{s,i} \frac{\partial c_{r,i}^f}{\partial r} \right) \right]. \quad (14)$$

The system of equations described in this section is a homogeneous system of partial differential equations. It can be used to calculate the increment/decrement of the fluctuations for given adsorption isotherms and equation of state.

#### 4. INCREMENT/DECREMENT OF FLUCTUATIONS. STABILITY CRITERIA

For simplicity we assume also that the disturbances vanish at the film periphery, i.e.  $h = p^f = v_r = v_z = 0$  at  $r = R$ . This assumption can be justified in view of the results of Gumerman & Homsy (1975) who found that the conditions assumed at the edge of the film do not significantly affect the predicted values of marginally stable film thickness.

Because of the cylindrical geometry and the conditions at the film ring, we can present the solution in the following form:  $(h, p_r^f, u, c_{r,i}^f) = (\tilde{h}, \tilde{p}_r^f, \tilde{u}, \tilde{c}_{r,i}^f) e^{\omega t} J_0(\alpha r)$ , where  $\alpha$  is the root of the zero order Bessel function,  $J_0(\alpha R) = 0$ , and  $\alpha^{-1}$  has a length dimension. In the above equations the tilde denotes the amplitude of the variables and  $\omega$  is increment/decrement of the fluctuations (stability factor).

After substituting the above solutions into the mass balance equation (13), for amplitudes of the fluctuations in surfactant concentrations in the reference phase the following relationships are obtained:

$$\tilde{c}_{r,i}^f = -\frac{\tilde{u}}{\alpha} b_i + \tilde{p}_r^f d_i, \quad b_i \equiv \frac{\Gamma_i}{\gamma_i} + \frac{c_{\infty,i}}{\gamma_i} \left( f_{s,i}'' - \frac{H}{2} f_{s,i}''' \right), \quad d_i \equiv \frac{c_{\infty,i}}{\eta \gamma_i} \left( f_{s,i} + \frac{H^3}{24} f_{s,i}''' \right), \quad (15)$$

where  $b_i$  and  $d_i$  are known parameters calculated from the basic (equilibrium) state.

We solve the stability problem using the assumption for long waves, i.e. the wave length is of the order of the film radius,  $\lambda \propto R$ . Therefore the surface viscosity effects compared to the elasticity effects can be neglected,  $[\text{surf. visc.}] / [\text{surf. elast.}] \propto \eta_s u / (R E_G) \ll 1$ .  $(\partial \Gamma / \partial c_i)_{\text{eq}}$  is much higher than the film thickness,  $H$ , for ionic surfactants. Hence, the effects from the deviation in the surface electric potential and charge are proved to be also negligible. Then after substitution of solutions the normal and tangential stress balance equations (10) are simplified to:

$$\tilde{p}_r^f \chi = \frac{\tilde{u}}{\alpha} kT \sum_{i=1}^n b_i f_{s,i}''' - \tilde{h} \left[ \left( \frac{\partial \Pi}{\partial H} \right) - \frac{\alpha^2 \sigma_a}{2} \right], \quad \tilde{p}_r^f H \zeta + \frac{2\pi}{\varepsilon} \rho_s^2 \tilde{h} = \frac{\eta \tilde{u}}{H \alpha} \xi. \quad (16)$$

In Eqs. (16)  $\chi$ ,  $\xi$ , and  $\zeta$  are dimensionless parameters, which are calculated from the equilibrium state. They are defined through the expressions:

$$\chi \equiv 1 + kT \sum_{i=1}^n d_i f_{s,i}''', \quad \zeta \equiv 1 + \frac{2kT}{H} \sum_{i=1}^n d_i f_{s,i}'' + \frac{2E_G}{H \Gamma_1} \sum_{i=1}^n \frac{\partial \Gamma_1}{\partial c_i} d_i f_{s,i}''',$$

$$\xi = \frac{h}{\eta} \sum_{i=1}^n b_i \left( kT f_{s,i}'' + \frac{E_G}{\Gamma_1} \frac{\partial \Gamma_1}{\partial c_i} \right). \quad (17)$$

Substituting the above solutions, Eqs. (15), and (16) into Eq. (14), the stability factor,  $\omega$ , is calculated to be:

$$\omega \zeta = \alpha^2 \frac{H^3}{12\eta} \left[ \left( \frac{\partial \Pi}{\partial H} - \frac{\alpha^2 \sigma_a}{2} \right) \zeta \Phi + \frac{2\pi \rho_s^2}{\varepsilon} \left( 1 + \chi \Phi - \frac{12kT}{H^3} \sum_{i=1}^n f_{s,i} d_i \right) \right]. \quad (18)$$

The dimensionless mobility function  $\Phi$  is calculated from the equilibrium state. It takes into account the influence of the interfacial properties on the surface mobility and is defined as



$$\Phi = \left[ \frac{12\eta}{H^2} + \frac{\xi}{\zeta} + \frac{24kT}{H^3} \left( \sum_{i=1}^n f_{s,i} b_i - \frac{\xi}{\zeta} \sum_{i=1}^n f_{s,i} d_i \right) \right] \left( kT\zeta \sum_{i=1}^n f_{s,i}'' b_i - \frac{\xi\chi}{\zeta} \right). \quad (19)$$

In the case of high amount of surfactants the interfaces become tangentially immobile and  $\Phi = 1$ . For nonionic surfactants the second term in the right hand side of Eq. (18) is equal to zero (the surface charge density is zero, i.e.  $\rho_s = 0$ ). Then, for tangentially immobile interfaces,  $\Phi = 1$ , and nonionic surfactants, the well known result from the literature is recovered (Ivanov, 1980),  $\omega = \alpha^2 H^3 (2\partial \Pi / \partial H - \alpha^2 \sigma) / 24\eta$ .

For illustration of the effects of ionic surfactants on the film stability we solve numerically Eq. (18) for a foam system stabilized by SDS. The Frumkin isotherm parameters are taken from Kralchevsky *et al.* (1999). The equilibrium parameters of the same system are presented in Fig. 2 (solid line).

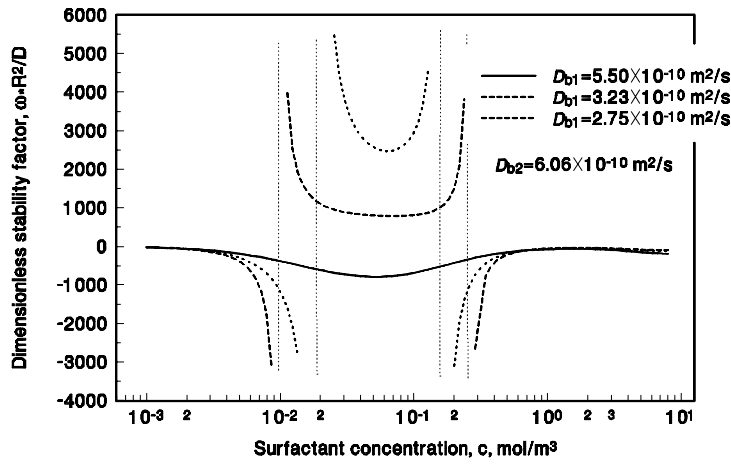


Figure 3 - Stability diagram: dependence of the increment/decrement,  $\omega R^2 / D$ , on the surfactant concentration,  $c$ .

We plot the dimensionless stability factor,  $\omega R^2 / D$ , vs. surfactant concentration,  $c_{1,\infty}$ , for different values of bulk diffusion coefficient of the surface active ion in Fig. 3. The negative values of the stability factor,  $\omega$ , refer to the region where the film is stable, and positive values correspond to unstable films. It is seen that at very low surfactant concentrations the film is stable. At such concentrations, first, the equilibrium film thickness is very large (see Fig. 2a) and the van der Waals attractive force is negligible, and second, the electrostatic interaction is very strong because of the almost fully overlapped EDL of the two surfaces (see Fig. 2b). With increase of the surfactant concentration the film becomes unstable, and at even higher concentrations - again stable, depending on the diffusion coefficient. It is important to note that in contrast to the particular case of nonionic surfactant, in the case of ionic surfactant solution the stability depends not only on the thermodynamic factors but also on the dynamic properties of the system. The higher the diffusion coefficient, the more stable the foam film. This is due to the faster diffusion process at higher  $D_{b1}$ , which leads to faster restoring of the equilibrium. The additional calculations show significant influence of surface diffusion coefficient and bulk viscosity. Also the increase of the film radius makes the film more unstable.

## 5. CONCLUSIONS

A theoretical model for calculation of the influence of surfactants and background electrolytes on the stability of plane-parallel, non-draining, liquid films is developed. It takes into account the effects of the electric potential, the surfactant distribution, the surface elasticity and viscosity, and the surface and bulk diffusion processes. The obtained relationship for increment/decrement,  $\omega$ , gives a possibility for estimating the rate of increasing/decreasing of the fluctuation amplitude. The stability region depends not only on the derivative of the disjoining pressure, but also on the fluctuations in the electric potential. The mobility of the interfaces accelerates the growth of the corrugations.

The obtained results can be used for computation of the critical thickness of liquid films stabilized by ionic surfactants and background electrolyte.

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