

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/40678399>

Streaming Potential Effect on the Drainage of Thin Liquid Films Stabilized by Ionic Surfactants

ARTICLE in *LANGMUIR* · JULY 2010

Impact Factor: 4.46 · DOI: 10.1021/la903593p · Source: PubMed

CITATIONS

9

READS

50

7 AUTHORS, INCLUDING:



Radomir I Slavchov

University of Cambridge

22 PUBLICATIONS 148 CITATIONS

[SEE PROFILE](#)



E. D. Manev

Sofia University "St. Kliment Ohridski"

80 PUBLICATIONS 1,516 CITATIONS

[SEE PROFILE](#)



Anh V. Nguyen

University of Queensland

152 PUBLICATIONS 2,198 CITATIONS

[SEE PROFILE](#)



Stoyan I Karakashev

Sofia University "St. Kliment Ohridski"

74 PUBLICATIONS 594 CITATIONS

[SEE PROFILE](#)

Streaming Potential Effect on the Drainage of Thin Liquid Films Stabilized by Ionic Surfactants

Roumen Tsekov,[†] Dilyana S. Ivanova,[‡] Radomir Slavchov,[†] Borjan Radoev,[†] Emil D. Manev,[†] Anh V. Nguyen,[§] and Stoyan I. Karakashev^{*,†}

[†]Department of Physical Chemistry, Sofia University, 1 James Bourchier Avenue, Sofia 1164, Bulgaria,

[‡]Faculty of Natural Sciences, Shumen University, 9712 Shumen, Bulgaria, and [§]School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

Received September 22, 2009. Revised Manuscript Received November 20, 2009

Dynamic effects originating from the electric double layers (EDL) are studied in thin liquid films (TLF) containing ionic and nonionic surfactants. To account for such effects, the EDL are to be incorporated into the differential equations describing the TLF drainage. Numerical simulations in the literature have shown that foam films containing ionic surfactants can drain at a slower rate than that predicted by the Reynolds equation (V_{Re}) which postulates rigid planar film surfaces. However, the physical reason of the trend has remained unclarified, and the numerical results have not been validated by any experimental data. In the present study, experiments on the drainage of planar foam films were conducted with the anionic surfactant sodium dodecylsulfate (SDS) in the presence of additional electrolyte (0.02 M NaCl) and with the cationic tetrapentylammonium bromide (TPAB). The obtained results are in accord with the numerical simulations from the literature ($V/V_{Re} < 1$). Such behavior was observed already in our preceding experiments on planar TLF with SDS without added electrolyte. These results were compared to the data of the experiments with TLF containing nonionic surfactant, and differences in the drainage pattern between ionics and nonionics were established. A new theoretical model was developed to account for the dynamic effects arising from EDL. According to the present model, the liquid outflow drags the bulk charges of EDL toward the film border, thus generating streaming potential (as in capillary tubes), which in turn brings the charges back toward the center to maintain the state of zero total electrical current. This creates reverse convection of the liquid near the surfaces, resulting in a velocity of film drainage smaller than V_{Re} . The present theory predicts kinetic dependence closer to the experiment than the Reynolds equation. The limitations of this new model are specified: it is valid for high ionic strength or low value of the surface potential.

1. Introduction

The drainage theory of thin liquid films (TLF)^{1–12} has been traditionally developed without considering the dynamic effects originating from the electrical double layer (EDL). Hence, the analytical equations based on this theory are valid for TLF with nonionic surfactants in the presence of background electrolyte, but in order to account for the action of EDL in the drainage of TLF, the Maxwell stress tensor and the electrokinetic effects originating from the very process of film drainage should be considered. Due to the complexity of the problem, the literature dedicated on this topic is very scarce.^{13–15} At the same time, EDL in dynamic conditions is widespread in nature: it is important for

the physics of foams, emulsions, and suspensions; for a number of industries, as, e.g., food industry, petroleum industry, mining, pharmacy, and medicine; in processes sustaining life, and so forth.

Numerical simulations of the drainage of TLF with ionic surfactant conducted recently¹⁵ have shown that such drainage can be slower than is predicted by the Reynolds equation^{16–19} ($V/V_{Re} < 1$), which postulates liquid flow between rigid planar film surfaces. The unexpected outcome ($V/V_{Re} < 1$) was explained there with the development of reverse currents close to the film surfaces and the very complex dynamics of EDL. However, the results were not validated by any experiment.

Numerical calculations have their advantages and disadvantages. For example, they give exact solutions of the equations, which are impossible to solve analytically. Concurrently, they require initial boundary conditions, which are difficult to define from the experiment, and are, for this reason, very rarely validated experimentally. In addition, they are much more difficult to operate with than the analytical models that are approximate, but easy to understand and utilize.

This work aims at offering a new analytical model for the drainage of TLF with ionic surfactants. The limitations of the model are outlined, and the model is validated experimentally.

*E-mail: fhsk@chem.uni-sofia.bg.

(1) Scheludko, A. *Kolloid Z.* **1957**, *155*, 39–44.

(2) Radoev, B.; Manev, Emil, D.; Ivanov, I., B. *Kolloid Z.* **1969**, *234*, 1039–1045.

(3) Radoev, B. P.; Dimitrov, D. S.; Ivanov, I. B. *Colloid Polym. Sci.* **1974**, *252*(1), 50–5.

(4) Ivanov, I. B.; Dimitrov, D. S. *Colloid Polym. Sci.* **1974**, *252*(11), 982–90.

(5) Malhotra, A. K.; Wasan, D. T. *Chem. Eng. Commun.* **1986**, *48*(1–3), 35–56.

(6) Davis, R. H.; Schonberg, J. A.; Rallison, J. M. *Phys. Fluids A* **1989**, *1*(1), 77–81.

(7) Sharma, A.; Ruckenstein, E. *Colloid Polym. Sci.* **1988**, *266*(1), 60–9.

(8) Hartland, S.; Jeelani, S. A. K. *J. Colloid Interface Sci.* **1994**, *164*(2), 196–298.

(9) Manev, E.; Tsekov, R.; Radoev, B. *J. Dispersion Sci. Technol.* **1997**, *18*(6 & 7), 769–788.

(10) Tsekov, R. *Colloids Surf., A* **1998**, *141*(2), 161–164.

(11) Tsekov, R.; Evstatieva, E. *Prog. Colloid Polym. Sci.* **2004**, *126*, 93–96.

(12) Ivanov, I. B. *Thin Liquid Films*; Marcel Dekker: New York, 1988.

(13) Felderhof, B. U. *J. Chem. Phys.* **1968**, *49*(1), 44–51.

(14) Valkovska, D. S.; Danov, K. D. *J. Colloid Interface Sci.* **2001**, *241*(2), 400–412.

(15) Valkovska Dimitrina, S.; Danov Krassimir, D.; Ivanov Ivan, B. *Adv. Colloid Interface Sci.* **2002**, *96*(1–3), 101–29.

(16) Stefan, M. J. *Sitzungsberichte der Mathematisch-naturwissenschaften Klasse der Kaiserlichen Akademie der Wissenschaften, II. Abteilung (Wien)* **1874**, *69*, 713–735.

(17) Reynolds, O. *Philos. Trans. R. Soc. London, Ser. A* **1886**, *177*, 157–234.

(18) Scheludko, A. *Adv. Colloid Interface Sci.* **1967**, *1*(4), 391–464.

(19) Scheludko, A.; Desimirov, G.; Nikolov, K. *Ann. Univ. Sofia, Fac. Phys. Math.* **1956**, *49*(2), 127–41.

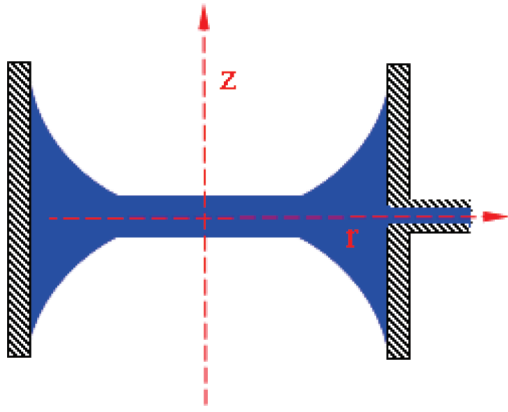


Figure 1. Sketch of a thinning foam film (not to scale).

2. Theoretical Model of Drainage of TLF Accounting for EDL

The Reynolds equation (see eq 18) was introduced by Scheludko^{18,19} to describe thinning of planar films with tangentially immobile surfaces (see Figure 1). It does not account for the effects on TLF thinning due to the presence of EDL on the film surfaces.

The electrostatic EDL-potential ϕ is assumed to be a strong function of the normal coordinate z and a weak function of the axial coordinate r (see Figure 1). During the film drainage, the charged liquid from the double layer moves toward the periphery of the film during the drainage, thus creating a streaming potential ϕ_0 . Hence, the total electrostatic potential ϕ contains an electrokinetic component ϕ_0 . Therefore, the EDL potential is expressed by $\phi - \phi_0$. One can operate with the potential on the middle plane ϕ_m , which is also a function on the radial coordinate. However, due to the superposition principle, one expects that the difference $\phi_m - \phi_0$ is independent of r , corresponding to unperturbed double layers. Hence, the choice to use ϕ_m or ϕ_0 is a matter of convenience and reflects only in the pre-exponential factor. Thus, the Poisson–Boltzmann equation²⁰ can be written by

$$\frac{\partial^2(\phi - \phi_0)}{\partial z^2} = -\frac{1}{\varepsilon_0 \varepsilon} \sum_i Z_i e c_{oi} \exp\left[\frac{-Z_i e(\phi - \phi_0)}{k_B T}\right] \quad (1)$$

where ε_0 and ε are the dielectric permittivities of free space and the medium, k_B and T are the Boltzmann constant and absolute temperature, Z_i and e are valence of the i -th ion and the charge of an electron and c_{oi} is the concentration of the i th ion in the periphery of the film.

We assume now a low value of the EDL potential ($\phi - \phi_0 < k_B T / Z_i e$) and thus linearize eq 1

$$\frac{\partial^2(\phi - \phi_0)}{\partial z^2} = \kappa^2(\phi - \phi_0) \quad (2)$$

where κ is the Debye constant. The solution of eq 2 can be expressed by:

$$\phi = \phi_0 + \frac{q_s}{\varepsilon_0 \varepsilon \kappa} \frac{\cosh(\kappa z)}{\sinh(\kappa h/2)} \quad (3)$$

where q_s and h are the surface charge density and the film thickness, respectively. The momentum balance equations are

expressed by their radial and normal components.¹⁴

$$\frac{\partial}{\partial r} \left(p + \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\partial \phi}{\partial z} \right)^2 \right) + \rho \frac{\partial \phi}{\partial r} = \eta \frac{\partial^2 v_r}{\partial z^2} \quad (4)$$

$$\frac{\partial}{\partial z} \left(p + \frac{\varepsilon_0 \varepsilon}{2} \left(\frac{\partial \phi}{\partial z} \right)^2 \right) + \rho \frac{\partial \phi}{\partial z} = 0 \quad (5)$$

where p is the hydrodynamic pressure across the film, η is the bulk viscosity, and v_r is the radial component of the liquid outflow velocity. The continuity equation is expressed by

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{\partial v_z}{\partial z} = 0 \quad (6)$$

where v_z is the normal component of the liquid outflow velocity.

The substitution of eq 3 in eqs 4 and 5 gives

$$\frac{\partial(p - \Pi_{el})}{\partial r} - q_s \kappa \frac{\cosh(\kappa z)}{\sinh(\kappa h/2)} \frac{\partial \phi_0}{\partial r} = \eta \frac{\partial^2 v_r}{\partial z^2} \quad (7)$$

$$\frac{\partial p}{\partial z} = 0 \quad (8)$$

where Π_{el} is the electrostatic disjoining pressure, which is expressed by

$$\Pi_{el} = \frac{q_s^2}{2\varepsilon_0 \varepsilon \sinh^2(\kappa h/2)} \quad (9)$$

The double integration of eq 7 along z gives the radial component of the velocity of liquid outflow v_r

$$v_r = \frac{z^2 - h^2/4}{2\eta} \frac{\partial}{\partial r} (p - \Pi_{el}) - \frac{q_s}{\eta \kappa} \frac{\cosh(\kappa z) - \cosh(\kappa h/2)}{\sinh(\kappa h/2)} \frac{\partial \phi_0}{\partial r} \quad (10)$$

where h is film thickness. In this equation, the gradient of the streaming potential $\partial \phi_0 / \partial r$ is unknown. The liquid outflow drives charges from the electrical double layer (EDL) toward the periphery of the film. To keep electroneutrality, however, reverse fluxes arise and bring the charges back. As a result, the total electrical current (toward the film periphery and back) is zero

$$\int_{-h/2}^{h/2} \rho v_r dz = 0 \quad (11)$$

The substitution of eq 10 in eq 11 yields an expression for the gradient of the streaming potential

$$\frac{\partial \phi_0}{\partial r} = \frac{2 \sinh(\kappa h/2)}{\kappa q_s} \frac{(\kappa h/2) \cosh(\kappa h/2) - \sinh(\kappa h/2)}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} \frac{\partial(p - \Pi_{el})}{\partial r} \quad (12)$$

Hence, one can substitute eq 12 in eq 10, which results in a new expression for the radial velocity of liquid outflow

$$v_r = \frac{1}{2\eta} \left\{ z^2 - \frac{h^2}{4} + \frac{4}{\kappa^2} \frac{\sinh(\kappa h/2) - (\kappa h/2) \cosh(\kappa h/2)}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} \right. \\ \left. [\cosh(\kappa z) - \cosh(\kappa h/2)] \right\} \frac{\partial(p - \Pi_{el})}{\partial r} \quad (13)$$

The substitution of eq 13 into the continuity eq 6 and integration on z gives the normal component of the velocity of the liquid

(20) Ohshima, H. *Surfactant Sci. Ser.*, **1998**, 76, (Electrical Phenomena at Interfaces), 57–85.

outflow

$$v_z = -\frac{1}{2\eta r} \frac{\partial}{\partial r} \left\{ r \left[\left(\frac{z^3}{3} - \frac{zh^2}{4} \right) + \frac{4}{\kappa^3} \frac{\sinh(\kappa h/2) - (\kappa h/2) \cosh(\kappa h/2)}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} [\sinh(\kappa z) - \kappa z \cosh(\kappa h/2)] \right] \frac{\partial(p - \Pi_{el})}{\partial r} \right\} \quad (14)$$

The integration of eq 14 in the limit from zero to $h/2$ gives the velocity of TLF drainage

$$\frac{\partial h}{\partial t} = \frac{1}{12\eta r} \frac{\partial}{\partial r} \left\{ rh^3 \left[1 - \frac{6}{(\kappa h/2)^3} \frac{[\sinh(\kappa h/2) - (\kappa h/2) \cosh(\kappa h/2)]^2}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} \right] \frac{\partial(p - \Pi_{el})}{\partial r} \right\} \quad (15)$$

For planar TLF ($\partial h/\partial r \ll 1$), the following eq 16 is obtained from eq 15

$$\frac{V}{V_{Re}} = 1 - \frac{6}{(\kappa h/2)^3} \frac{[\sinh(\kappa h/2) - (\kappa h/2) \cosh(\kappa h/2)]^2}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} \xrightarrow{\kappa h/2 \gg 1} 1 - \frac{12}{\kappa h} \quad (16)$$

where V_{Re} is the Reynolds velocity.

Equation 16 can also be expressed in the form

$$-\frac{dh}{dt} = \frac{2h^3(P_\sigma - \Pi)}{3\eta R^2} \left\{ 1 - \frac{6}{(\kappa h/2)^3} \frac{[\sinh(\kappa h/2) - (\kappa h/2) \cosh(\kappa h/2)]^2}{\cosh(\kappa h/2) \sinh(\kappa h/2) - \kappa h/2} \right\} \quad (17)$$

where $\Pi = \Pi_{el} + \Pi_{vw}$ is the total disjoining pressure, Π_{vw} is the van der Waals disjoining pressure, $P_\sigma = 2\sigma/R_c$ is the capillary pressure, R is the film radius, σ is the surface tension, and R_c is the radius of the capillary tube, in which the film is formed.

If the expression in the brace on the right-hand side of eq 17 equals unity, the Reynolds equation is obtained (see eq 18). The latter is an analogue of eq 17, which does not account for the streaming potential

$$V_{Re} = -\frac{dh}{dt} = \frac{2h^3(P_\sigma - \Pi)}{3\eta R^2} \quad (18)$$

Equations 16 and 17 are valid for planar TLF with tangentially immobile surfaces and low surface potentials. In addition, the diffusion potential, originating from the difference in the diffusion coefficients of the diverse ions, is neglected. In this sense, eqs 16 and 17 are approximate. The requirement for zero total electric current is fulfilled by the reverse convection bringing the ions back toward the film center.

3. Numerical Solution

Equation 17 was numerically integrated to obtain the transient film thickness using the fourth-order Runge–Kutta algorithm.

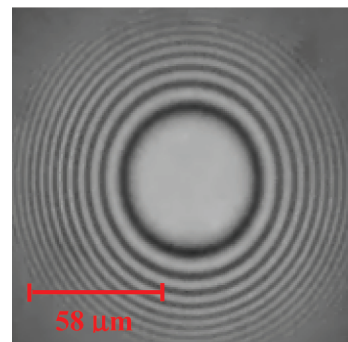


Figure 2. Interferographic image of a planar foam film containing 1×10^{-6} M SDS + 0.02 M NaCl.

A program was written using the VBA (Visual Basic for Application) programming language available in Microsoft Excel. The disjoining pressures in eqs 16 and 17 are calculated similarly to ref 21. As far as the basic part of the experiment is performed on thin films of relatively high ionic strength (0.02 M NaCl), the electrostatic disjoining pressure is negligible. Yet, the presence of EDL, despite being significantly suppressed, results in electrokinetic effects by means of streaming potential that creates reverse fluxes.

4. Experimental Section

Experiments on planar TLF drainage were conducted with the anionic surfactant sodium dodecylsulphate + 0.02 M NaCl in the concentration range (1×10^{-6} M) – (1×10^{-3} M) ($\text{cmc} = 10^{-3}$ M), with the cationic surfactant tetrapentyl ammonium bromide in the concentration range (1×10^{-5} M) – (1×10^{-2} M) and with the nonionic surfactant tetraethylene glycol octylether (C_8E_4) + 0.02 M NaCl in the concentration range (1×10^{-5} M) – (1×10^{-2} M) ($\text{cmc} = 7.5 \times 10^{-3}$ M). All these chemicals were purchased from Sigma Aldrich Corporation. In order to avoid effects caused by thickness inhomogeneities on the rate of thinning,^{9,22} small films ($R \leq 50 \mu\text{m}$) were as a rule investigated. As an illustration, an interferographic image of a plane-parallel foam film containing 1×10^{-6} M SDS + 0.02 M NaCl is presented in Figure 2.

Marangoni numbers of foam films with SDS + 0.02 M NaCl and TPeAB have significant values ($\text{Ma} > 10^5$ in the case of SDS + 0.02 M NaCl; $\text{Ma} > 10^3$ in the case of TPeAB). Hence, the assumption for immobile film surfaces in the present experiment is justified.

Sodium dodecyl sulfate was purified by recrystallization from ethanol. The surface tensions of the solutions were measured and the Gibbs elasticity and the adsorption length were calculated.

The microinterferometric method was used to determine the behavior of the transient foam films. The detailed description of the experimental setup has been reported previously (see, e.g., refs 23–25) and is not presented in full here. Briefly, the apparatus consists of a glass cell for producing horizontal foam films normal to gravity. First, a droplet of surfactant solution was formed inside the film holder. Then, the amount of liquid was regulated by means of a gas-tight microsyringe connected to the film holder through a glass capillary. Finally, a microscopic film was formed between the apexes of the double-concave meniscus by pumping out the liquid from the drop. A metallurgical inverted microscope was used for illuminating and observing the film and

(21) Karakashev, S. I.; Nguyen, A. V. *Colloids Surf., A* **2007**, 293, 1–3.

(22) Radoev, B.; Scheludko, A.; Manev, E. *J. Colloid Interface Sci.* **1983**, 95(1), 254–65.

(23) Exerowa, D.; Kruglyakov, P. M. *Foam and Foam Films: Theory, Experiment, Application*; Marcel Dekker: New York, 1997; p 796.

(24) Karakashev, S. I.; Nguyen, A. V. *Colloids Surf., A* **2007**, 293, 229–240.

(25) Manev, E. D.; Nguyen, A. V. *Int. J. Miner. Process.* **2005**, 77(1), 1–45.

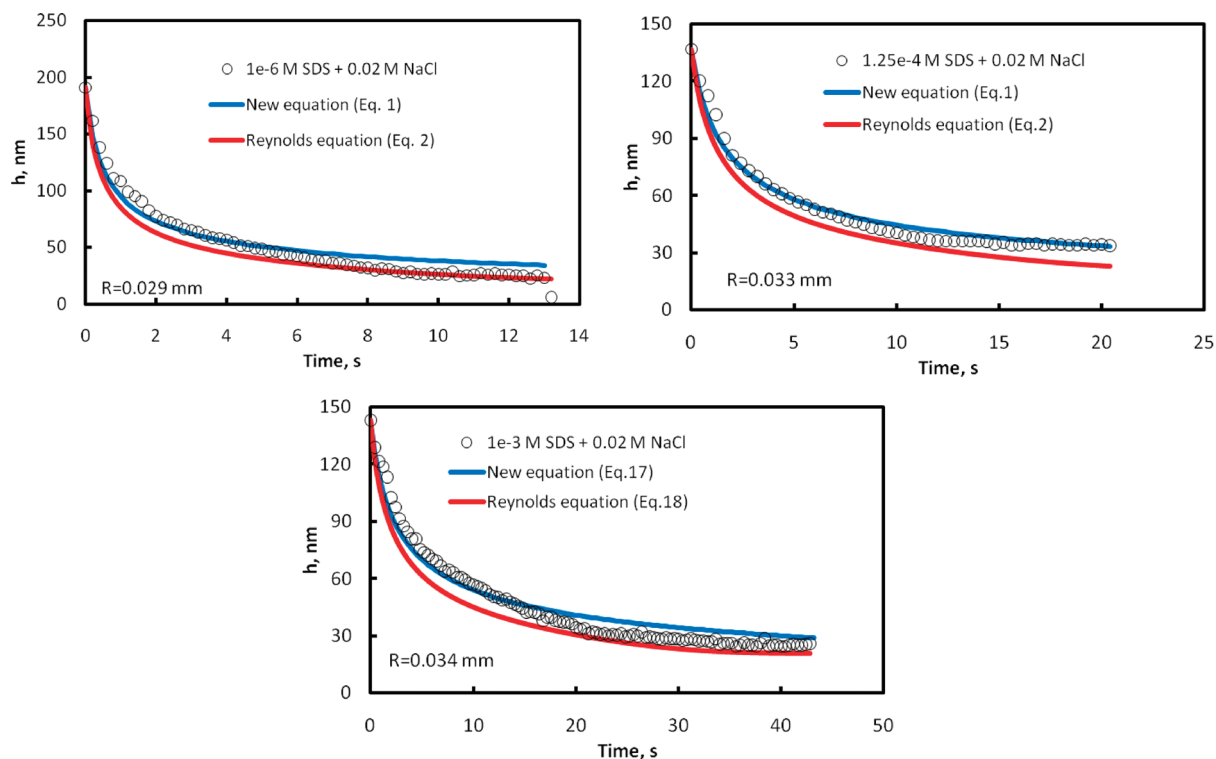


Figure 3. Illustration of the model predictions (red curve – eq 18, blue curve – eq 17) and the experimental results (points) for the transient thickness of SDS + 0.02 M NaCl foam films.

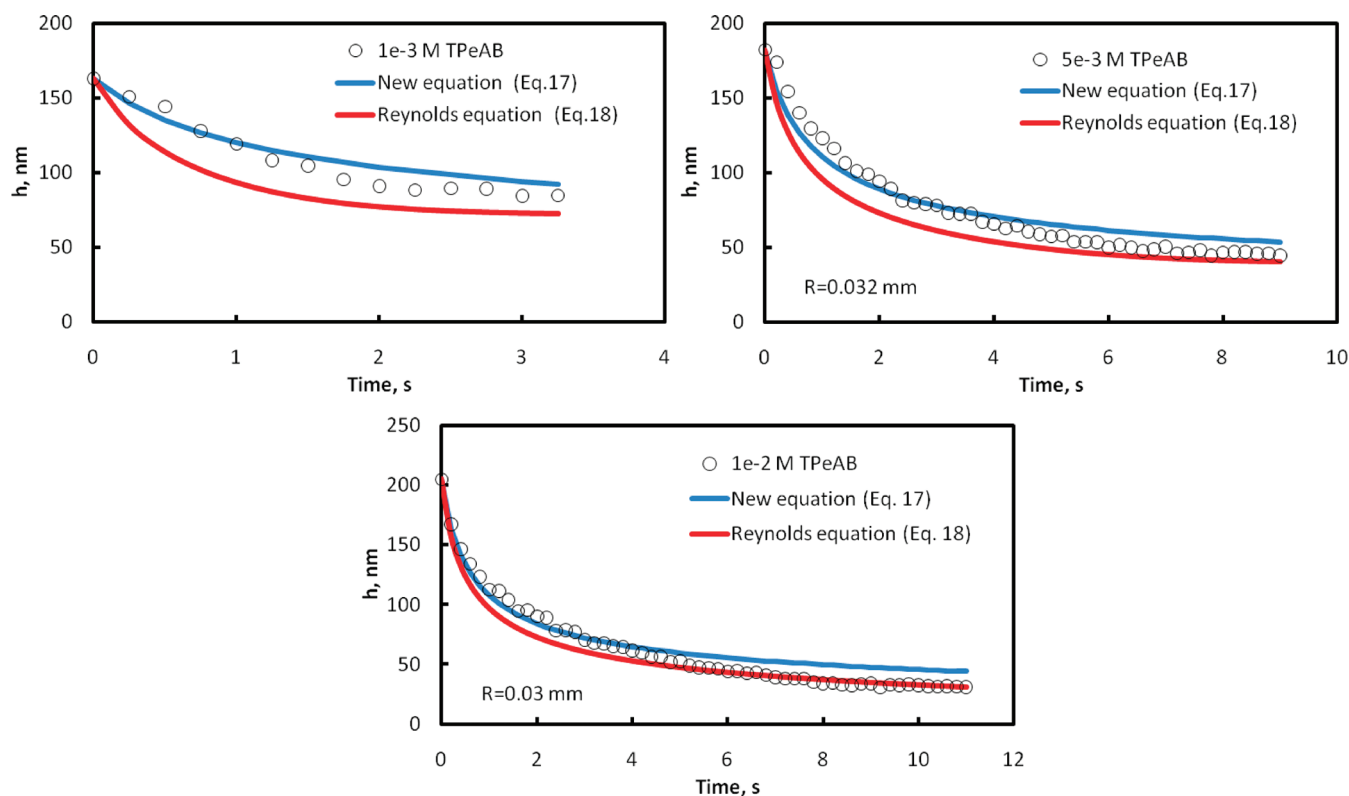


Figure 4. Illustration of the model predictions (red curve – eq 18, blue curve – eq 17) and the experimental results (points) for the transient thickness of TPAB foam films.

its interference fringes (the Newton rings) in reflected light of $\lambda = 546$ nm wavelength and a digital camera system connected with a computer for storage of the data. The experiments were

conducted at constant temperature of 25 °C via water bath thermostat. This eliminated the temperature gradients in the Scheludko cell. In this mode, the film radii were maintained

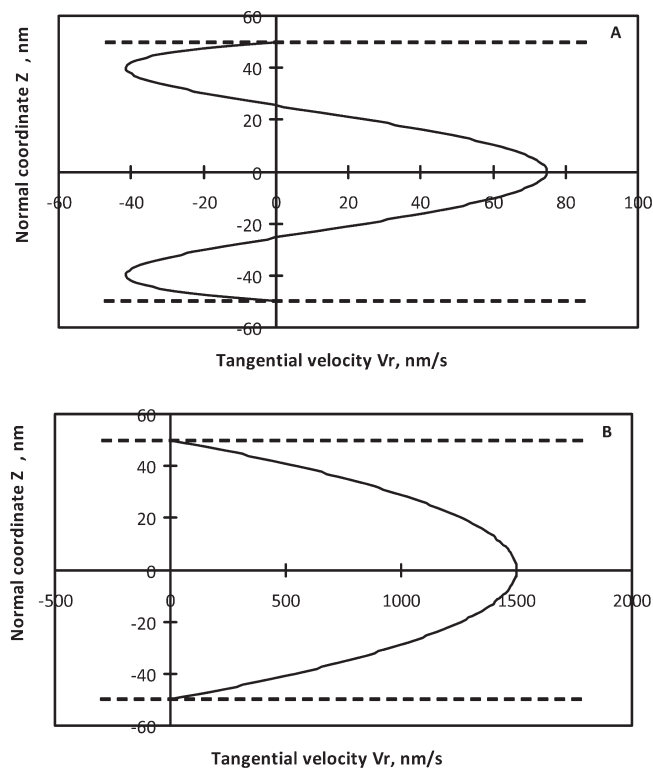


Figure 5. Illustration of the tangential velocity of liquid outflow at film drainage accounting for the streaming potential (eq 17), A; and according to the Reynolds equation (eq 18), B. The interrupted lines signify the film surfaces.

strictly constant during film drainage, which was visually controlled and recorded. The interferograms were processed offline using the *ImageJ* software for image processing delivering the pixel signal from a given small area. Thus, the frames were extracted from the recorded movie in time resolutions up to 0.4 s. The film radii were measured in the series of sequent frames, and the averaged film radius was derived with accuracy of $\pm 1 \mu\text{m}$.

5. Results and Discussion

The experiment was aimed at investigating the effects of EDL on the drainage of planar foam films; hence, foam films of radii up to $50 \mu\text{m}$ were studied. The theoretical curves derived from the Reynolds equation (eq 18) and the present model (eq 17) were compared with the experimental data. The comparison is presented in Figures 3 and 4.

It is evident from the figures that the foam films drain more slowly than predicted by the Reynolds equation and the model developed in the present study agrees better with the experimental data, although not perfectly. The latter fact may be due to the number of approximations assumed in the course of deriving the analytical solution. For example, while assuming that the ions are brought to the film center by reverse fluxes, generated by the streaming potential, the backward diffusion of the charges toward the film center was neglected in the model (see Figure 5). The tangential velocity profiles of the liquid outflow v_r according to the two models are presented schematically in Figure 5. It should be stressed again here that the conventional theory of TLF drainage does not assume dynamic effects originating from EDL.

Furthermore, the drainage pattern predicted by the new model for films with ionic surfactants is supported by the results obtained with nonionic surfactants. Figure 6 presents the comparison

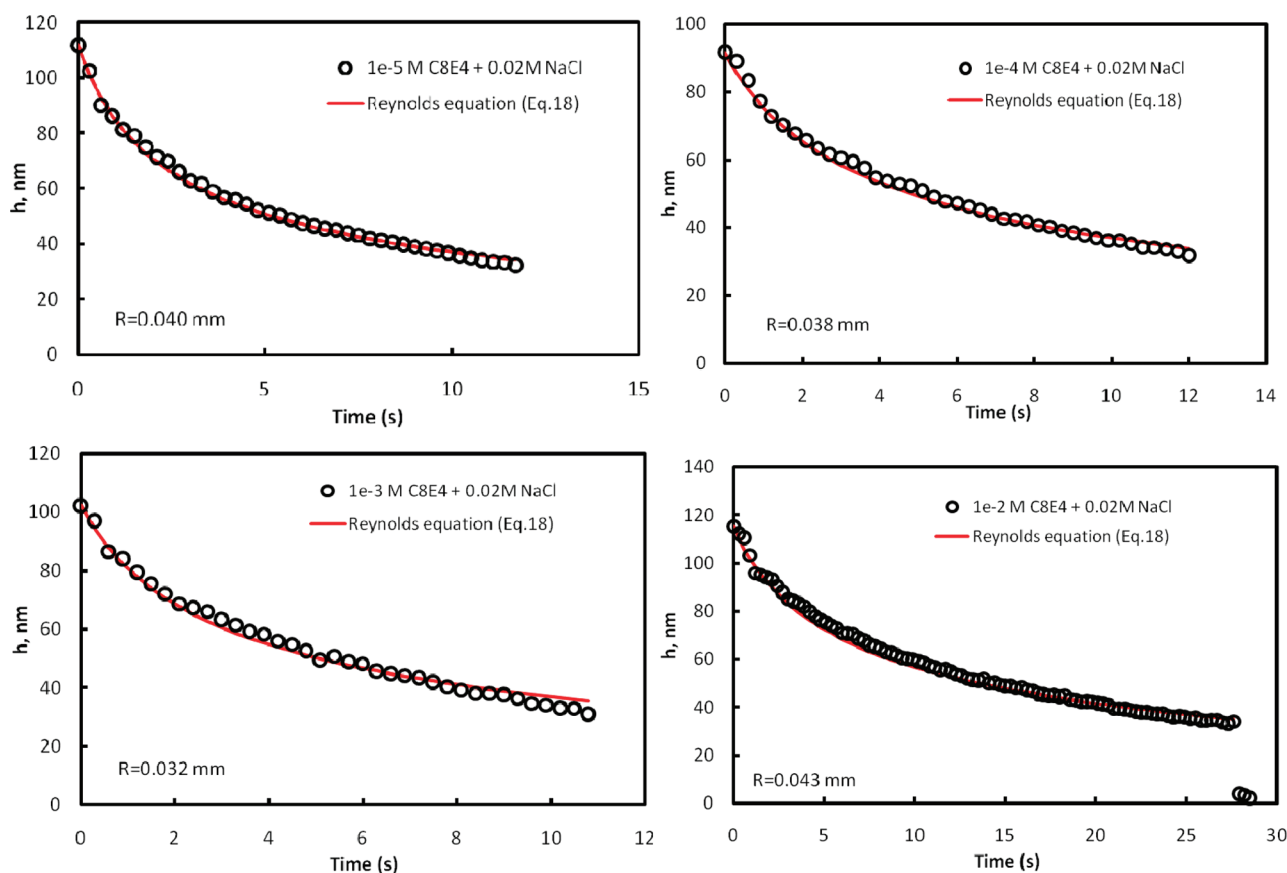


Figure 6. Comparison of the Reynolds equation predictions (red curve) and the experimental results (points) for transient thickness of $\text{C}_8\text{E}_4 + 0.02 \text{ M NaCl}$ foam films.

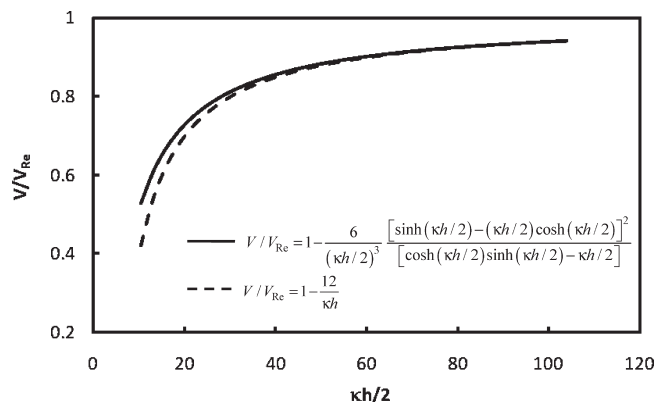


Figure 7. V/V_{Re} vs $\kappa h/2$ according to the complete and simplified equations (see eq 16).

of the experimental data for foam films with C_8E_4 in the presence of 0.02 M NaCl with the kinetic curves predicted by the Reynolds equation (eq 18). Basically, the conventional drainage theory for planar TLF accounts for the film surface mobility, which is controlled by the Marangoni effect,¹⁸ the adsorption³ and surface diffusion of surfactant, and the surface viscosity.^{4,21} The Marangoni effect is dominant among the factors controlling the motion of the film surfaces. In most cases, the surfaces become practically immobile even at very low levels of surfactant concentration. Hence, such films from diluted aqueous solutions of nonionic surfactants drain according to the Reynolds equation (eq 18) if they are planar. This is evident from Figure 6 for the aqueous foam films of small radii (≤ 0.05 mm) with $\text{C}_8\text{E}_4 + 0.02$ M NaCl and such a result is not surprising.

The new model (see eq 16) can be reduced to the simple formula $V/V_{\text{Re}} = 1 - 12/\kappa h$ at high $\kappa h/2$ values (see Figure 7).

Figure 7 presents the comparison between the complete and the simplified kinetic equations (see eq 16) as a function of $\kappa h/2$. It is evident that above $\kappa h/2 = 40$ the formulas practically coincide. Consequently, the simplified formula $V/V_{\text{Re}} = 1 - 12/\kappa h$ is valid for relatively thick films.

Being based on the solution of the linearized Poisson–Boltzmann equation, the analytical drainage equation (see eq 16) assumes low values of the surface potential. Hence, it is

valid for foam films with considerably suppressed EDL. The application of this equation to TLF with developed (nonsuppressed) EDL causes overestimation of the streaming potential values and, hence, significantly slower drainage than is established experimentally.

6. Conclusions

This study develops an analytical kinetic equation for the drainage of TLF with ionic surfactant and validates it by experiments. This new kinetic equation is based on certain approximations: low values of the surface potential; no backward diffusion of the ions from the film periphery toward its center; tangentially immobile, rigid, and planar film surfaces. The equation was validated with drainage experiment on foam films with the anionic surfactant SDS + 0.02 M NaCl and the cationic surfactant TPAB. The validation of this new equation showed better agreement with the experimental data than the Reynolds equation. The latter predicts faster drainage than is experimentally established. A second set of experiments on drainage of planar foam films with nonionic surfactant $\text{C}_8\text{E}_4 + 0.02$ M NaCl was conducted. It was shown that in the latter case the films drain according to the conventional theory.

One could pose a question regarding why TLF with nonionic surfactants does not exhibit identical effect to TLF with ionic surfactant if EDL under dynamic conditions is present in both cases. It is generally assumed that TLF with nonionic surfactants exhibits negative potential of the film surfaces, due to the “adsorption” of hydroxyl ions (OH^-) from the water.²³ However, both hydroxyl (OH^-) and hydroxonium (H_3O^+) ions are attracted by the bulk water due to their positive Born energies. Yet, OH^- ions are located closer to the film surfaces than H_3O^+ . In fact, both H_3O^+ and OH^- ions are driven away toward the film periphery during its drainage, while the real surface potential remains zero. Hence, there is no physical reason for streaming potential arising during the drainage of TLF in the presence of nonionic surfactants.

Acknowledgment. Stoyan Karakashev gratefully acknowledges the EC “Marie Curie Actions” for the financial support through DETLIF – Project No. 200688/2009.