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ANOMALOUS DRAINAGE OF NANOFILMS FROM CONCENTRATED NACL SOLUTIONS OF TETRAETHYLENE GLYCOL OCTYL ETHER (C8E4)

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Abstract. The drainage of planar foam nanofilms, stabilized by tetraethylene glycol octyl ether (C_8E_4) in aqueous solutions of NaCl was studied. The experiments on foam nanofilm drainage were performed at three different NaCl concentrations – 0.02 M, 0.2 M and 2 M. In each one of these salt solutions the variation of the surfactant (C_8E_4) concentration was within the range of 10^{-6} – 10^{-3} M. It was established that at 0.02 M NaCl the nanofilms drain in accord with Reynolds equation. At 0.2 M NaCl small deviations from the theoretical predictions were observed in some cases. At 2 M NaCl the nanofilms drain substantially slower than the prediction of the Reynolds equation. In addition, it was found that the overall dependence nanofilm thickness versus time became linear instead of exponential one at 10^{-4} M and 10^{-3} M C_8E_4. The latter is unexpected results because it shows change in the very regime of drainage of the foam nanofilm.

Keywords: nanofilms, foam film drainage, thin liquid films, salt solutions, non-ionic surfactants

Introduction

The kinetics of nanofilms drainage is part of the overall behaviour of gas and oil emulsions, foams, suspensions, etc, despite being under dynamic or static conditions (Binks, 1998; Exerowa & Kruglyakov, 1998; Ivanov, 1988; Nguyen & Schulze, 2003; Oron et al., 1997). Hence, the nano-films and their drainage behaviour were investigated in many aspects. For example, it was established that planar foam nanofilms, stabilized by non-ionic surfactants, and with immobile surfaces drain according to the Reynolds equation (Scheludko, 1967). The thinning of planar films with mobile surfaces was described by Barber & Hartland (1976), Ivanov & Dimitrov (1974) and Radoev et al. (1974). The drainage of non-planar films was described by Manev et al. (1997), Radoev et al. (1983), Sharma & Ruckenstein (1988), Tsekov & Evstatieva (2004). Tsekov et al. (1997) and Tsekov & Ruckenstein (1994). In addition, numerical simulations describing the evolution of asymmetric nanofilms were performed by Joye et al. (1996), Li (1996) and Manica et al. (2007; 2008). All these theoretical predictions were based on the lubrication and quasi-steady approximations. In addition, it was assumed that the charges of the electrical double layer (EDL) within the nanofilms are immobile during the drainage thus excluding possible electrokinetic effects, which might occur during the drainage. It was established recently (Tsekov et al., 2010; Valkovska & Danov, 2001) that planar foam films stabilized by ionic surfactants drain slower than the prediction of the Reynolds equation. It was explained with emergence of streaming potential along the film radius, which generates reverse to the overall liquid outflow fluxes close to the film surfaces. This converged with the electro-Marangoni effect in a case when the nanofilms surfaces are mobile (Karakashev & Tsekov, 2011).

The behaviour of dispersed systems in highly concentrated solutions of inorganic salts was intensively investigated in the last decades (Craig et al., 1993; Karakashev et al., 2008; Yaminski et al., 2010). The drainage of such nanofilms in presence of highly concentrated salt solutions was not investigated till present. This paper aims to study the drainage of foam nanofilms in highly concentrated salt solution.

Experimental

Experiments on drainage of planar foam nanofilms were conducted with the nonionic surfactant tetraethylene glycol octyl ether (C_8E_4) in the concentration range $10^{-6} – 10^{-3}$ M at three different concentration of NaCl – 0.02 M, 0.2 M, and 2 M. In order to avoid effects caused by thickness inhomogeneities on the rate of thinning (Manev et al., 1997; Radoev et al., 1983), small films ($R \leq \mu$m) were as a rule investigated. The surface tensions of the solutions were measured by the Wilhelmi plate method. The microinterferometric method was used to determine the behavior of the transient foam films. The full description of the experimental set-up was reported previously (Exerowa & Kruglyakov, 1997; Karakashev & Nguyen, 2007) and is not presented in full here (Fig.1).

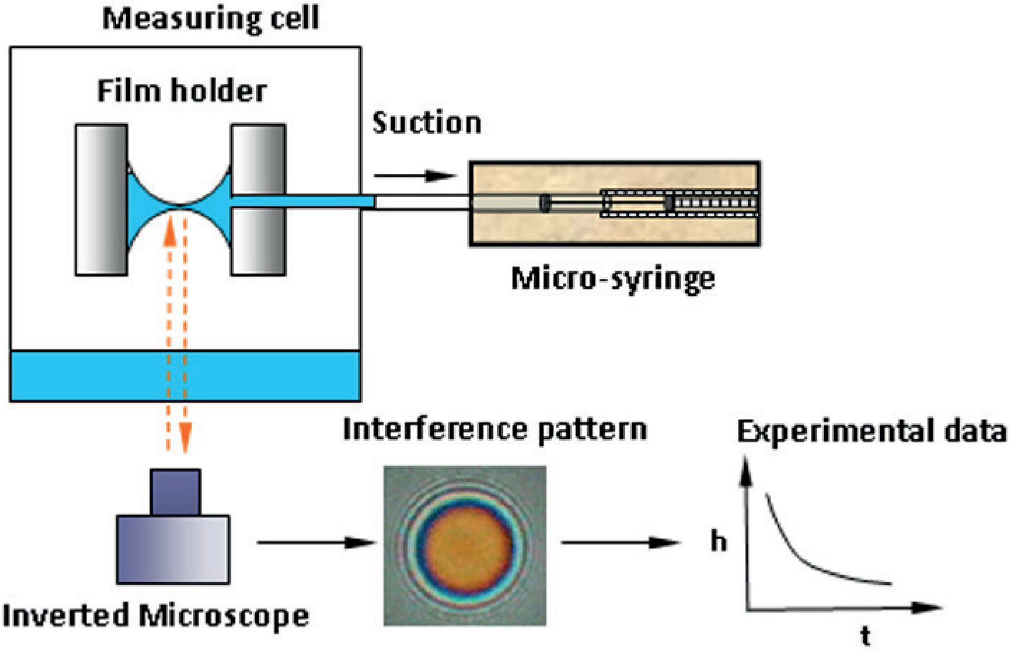

Fig. 1. Interferometric setup for studying of thin liquid films

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 gastight micro-syringe connected to the film holder through a glass capillary. Finally, a microscopic nanofilm 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 its interference fringes (the Newton rings) in reflected light of $\lambda = 546$ nm wavelength and a digital camera system connected with computer for storage of the data. The interferograms were processed offline using the “Image J” software for image processing delivering the pixel signal from a given small area. Thus the frames were extracted from the recorded movie. The film radii were measured in the series of sequent frames of and the averaged film radius was derived with average deviation in the range of ±1 μm. The experimental data film thickness versus time was compared with the prediction of the Reynolds equation:

$$V_{\mathrm{Re}} = -\frac{dh}{dt} = \frac{2h^3}{3\mu R_f^2}\left(P_\sigma - \Pi\right) \tag{1}$$

where h and t are nanofilm thickness and time, μ is bulk viscosity, R_f is film radius, $P_\sigma = 2\sigma / R_c$ is the capillary pressure, σ is surface tension, R_c is the radius of the film holder, where the nanofilm is formed in, Π is total disjoining pressure composed by electrostatic and van der Waals components (Ivanov, 1988).

Results and discussion

The experimental and theoretical data on nanofilms drainage at 0.02 M NaCl is presented in Fig.2.

It is apparent the coincidence between experiment and theory in Fig. 2. It should be noted here that that at 10^{-6} M C_8E_4 the nanofilms drain a bit faster than the prediction of the Reynolds equation due to the nano-film surface mobility. The experimental and theoretical data on nanofilms drainage at 0.2 M NaCl is presented in Fig.3.

One can see some deviations between theory and experiment in Fig. 3. These deviations are expressed in slower drainage than the prediction of Reynolds equation at certain surfactants concentrations.

The experimental and theoretical data on nanofilms drainage at 2 M NaCl is presented in Fig.4.

At 2 M NaCl (see Fig.4) the foam nanofilms in the whole concentration range of C_8E_4 drain slower than the prediction of Reynolds equation. In addition, one can see that the very regime of nanofilms drainage is linear instead of exponential (see Figs. 2 and 3). The latter means change in way the nanofilms drains. Obviously unknown phenomenon occurs thus making the foam nanofilms behaves in this manner. One could explain the slower drainage with the emergence of streaming potential effect similar to drainage of nanofilms with ionic surfactants (Tsekov et al., 2010). However, the streaming potential effect weakens upon the increase of the ionic strength. At 2 M NaCl the streaming potential effect should be negligible. We call upon further investigation of these interesting effects.

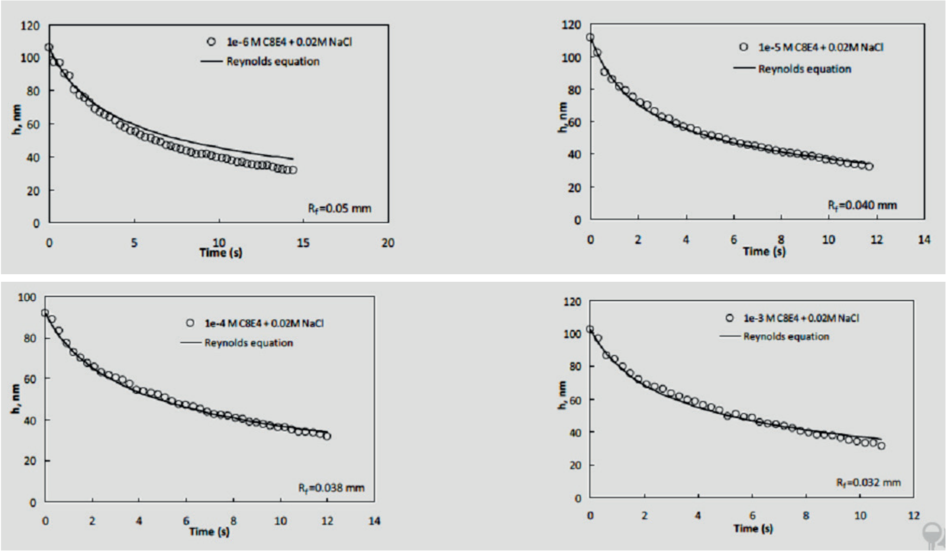

Fig. 2. Experimental and theoretical (Reynolds equation) drainage of planar nanofilms containing C_8E_4 at 0.02 M NaCl

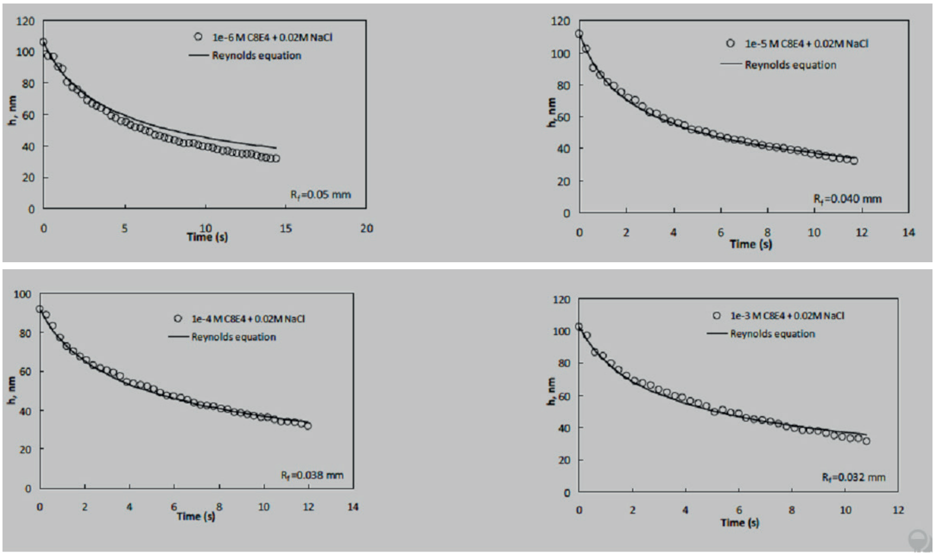

Fig. 3. Experimental and theoretical (Reynolds equation) drainage of planar nanofilms containing C_8E_4 at 0.2 M NaCl

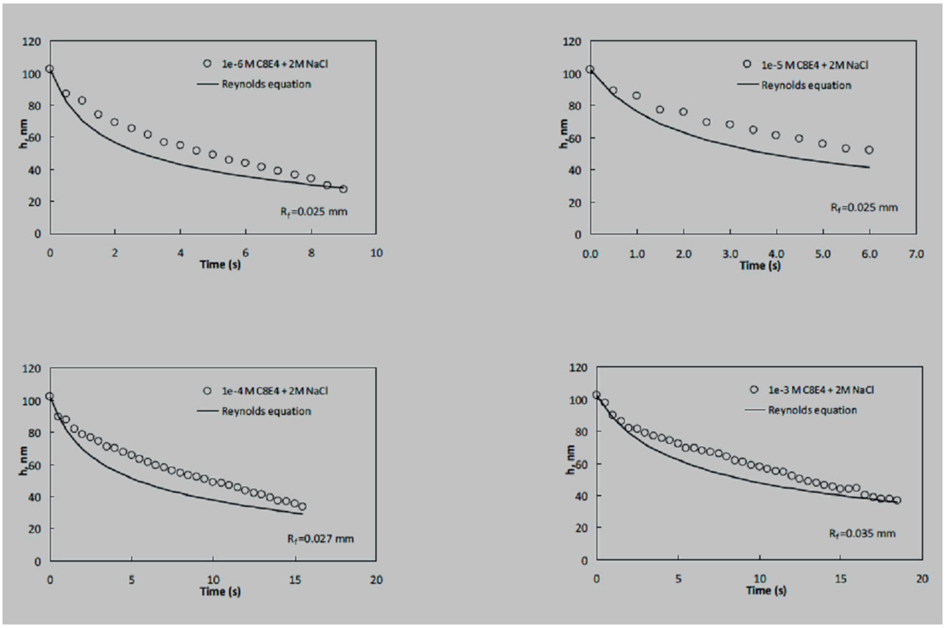

Fig. 4. Experimental and theoretical (Reynolds equation) drainage of planar nanofilms containing C_8E_4 at 2 M NaCl

Conclusions

This paper reports about an interesting effect emerging during the drainage of planar foam nanofilms stabilized by non-ionic surfactant C_8E_4 at three different concentrations of NaCl – 0.02 M, 0.2 M, and 2 M. It was shown, that at 0.02 M NaCl the foam films drainage follows the prediction of the Reynolds equation. Deviations from the theory start upon increase of NaCl concentration (Fig.3). At the highest concentration of NaCl the foam nanofilms drain linearly and slower than the prediction of the Reynolds equation. This establishment cannot be explained with the present theoretical models.

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