

Reply to Comment on “Hydrophobic Forces in the Foam Films Stabilized by Sodium Dodecyl Sulfate: Effect of Electrolyte” and Subsequent Criticism

Introduction

The comments cited in the title¹ are mostly focused on a discussion and criticism of a previous article by Wang and Yoon.² Stubenrauch et al.¹ also cited our study,³ presenting its contents in an incorrect way. Here, we restrict ourselves to a brief response to the comments regarding our article. The authors of ref 1 write “The long-range hydrophobic force concept was also used to describe film thinning, that is, drainage. In refs 3–5, it was found that the Reynolds equation (in which the driving force for the drainage is given by the disjoining pressure) does not describe the drainage: the foam films drain faster than theoretically predicted. Attributing the faster drainage to an attractive long-range hydrophobic force and extending the DLVO expression with the respective term for the long-range hydrophobic force indeed leads to a good fit of the experimental data. However, the Reynolds equation was derived for film thinning between flat solid surfaces. Thus, the assumption of tangentially immobile surfaces is incorrect in the case of many foam films as was shown in ref 6. The lower the surfactant concentration and the thicker the film, the more pronounced is this effect.^{6,7} As the foam films studied by the authors are indeed stabilized by low surfactant concentrations and as they are relatively thick, the accelerated film thinning could be partly due to the convective surface motion of the surfactant (Marangoni effect).”

First, in our article³ we report and interpret data for the dependence of the critical thickness of film rupture, h_{cr} , on the film radius, R (see Table 1 and Figure 5 therein) rather than data for the dependence of the film thickness, h , on time, t (i.e., for the process of film drainage). Physically, these are two quite different dependencies.

Second, in our article the dependence $h_{cr}(R)$ is interpreted by means of stability analysis of liquid-film breakup based on the theory of the growth of fluctuation capillary waves⁸ (see eqs 8–10 and 13–15 in ref 3) rather than the Reynolds equation, which describes the drainage of plane-parallel films.

We applied the latest and the most complete version of the theory of film breakup by capillary waves,⁸ coauthored by one of us (K.D.D.), which takes into account all effects related to the mobility of the film surfaces, including the surface dilatational elasticity (the Marangoni effect), the surface convection and diffusion, the effects of bulk and surface viscosities, and the

exchange of surfactant molecules between the bulk and the film surfaces. This theory has two versions: with linear and nonlinear stability analysis.⁸ The theory was tested against available experimental data, and very good agreement was found without using any adjustable parameters.^{8,9} However, our quantitative analysis of the data for the rupture of films at low SDS concentrations³ showed that the measured greater values of h_{cr} cannot be attributed to the effects of surface mobility. In the considered case, it turned out that data processing by means of the full computer program taking into account all mobility effects⁸ gives the same result as if these effects are switched off (i.e., the surfaces are tangentially immobile). A closer inspection of the equations showed that the growth of capillary waves (unlike film drainage) is insensitive to the effects of the surface mobility of the surfactant, at least for the parameter values corresponding to the investigated system.

Thus, the application of the most complete and quantitative theory of film rupture by the growth of capillary waves showed that the measured greater (than expected on the basis of the van der Waals attraction) critical thicknesses of film rupture cannot be explained as an effect of surface mobility. However, when we hypothesized that an additional attractive force is acting in the film and if we incorporate in the computer program the theoretical expression for the hydrophobic force due to Eriksson et al.,¹⁰ we were able to fit the data very well, and the decay length of this additional attraction, 15.8 nm for all three studied concentrations, coincided with the value obtained in ref 10 for liquid films sandwiched between two hydrophobic solid surfaces. A similar result was obtained by Paunov et al.¹¹ for emulsion systems. Without being an unequivocal proof for the existence of such hydrophobic attraction, our results indicate that it could be at least one of the possible explanations.

Finally, the statements in ref 1 that the apparent effect of the hydrophobic surface force can be quantitatively explained by adjusting the value of the surface electric potential do not refer to our study, where the solutions contain 0.3 M NaCl. At such a high ionic strength, the double-layer repulsion is completely suppressed at distances of 26–40 nm, corresponding to the range of our experimental critical thickness. Nevertheless, if we assume that some traces of electrostatic repulsion still exist, then we would have to assume the presence of even a stronger additional attraction in order to obtain quantitative agreement between theory and experiment.

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