A disjoining pressure study of foam films stabilized
by tetradecyl trimethyl ammonium bromide $C_{14}TAB$

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In order to find out the electrolyte concentration at which an NBF is formed, measurements at different electrolyte concentrations were carried out. As is seen in Fig.A1, at 0.1 M and 0.4 M NaCl it is still a CBF that is formed. Thus the electrolyte concentration required to form an NBF is between 0.4 M and 1 M. It would be interesting to specify the exact electrolyte concentration. This, however, was not the aim of the present work so that we did not carry out these time consuming measurements.

Due to the higher ionic strength the Π–h curves obtained at 0.1 and 0.4 M, respectively, are steeper and the films are thinner than those of the corresponding salt-free system. However, in contrast to the latter, the Π–h curves cannot be described with the DLVO theory, an observation that is usually made. The DLVO model is known to be reasonably accurate for low electrolyte concentrations where electrostatic forces dominate, but fails at high electrolyte concentrations (>0.05 M) where electrostatic forces are screened and dispersion forces are increasingly important.[i]

The origin of the short-range forces stabilizing NBFs of ionic surfactants is still under discussion. Steric (entropic) repulsion—as accepted for non-ionic surfactants due to their large headgroups—is questionable as the headgroups of ionic surfactants are usually not very large. One explanation is the adsorption of highly hydrated counterions at the interface, which results in repulsive forces because a further approach of the interfaces would require dehydration of these ions.[ii,iii] Another explanation was published only recently. According to Faraudo *et al.*, the origin of the repulsion is not entropic but electrostatic in nature.[iv,v] However, this electrostatic repulsion is not the "classical" repulsion observed between equally charged surfaces, but is caused by highly polarized water next to the charged surfactant layer. Thus it is not the repulsion between ions but between highly polarized dipoles that is considered. Note that the latter interactions are short-range compared to ion–ion interactions thus explaining its validity for NBF.
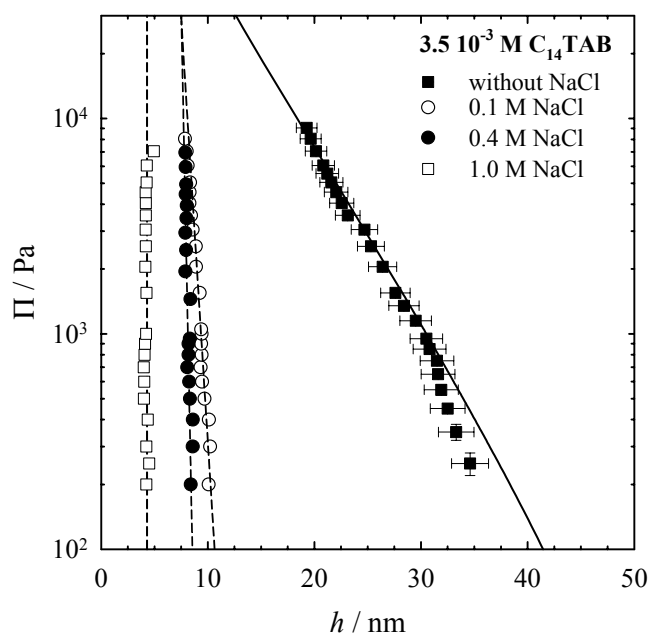
Fig.A1: Disjoining pressure Π as a function of the film thickness h for 3.5 10^{-3} M $C_{14}TAB$ in different salt solutions, namely 1.0 M NaCl (□), 0.4 M NaCl (●), 0.1 M NaCl (○), and without additional electrolyte (■). A CBF is formed for the solution without NaCl and for the two lower salt concentrations, whereas for the highest NaCl concentration only an NBF was observed. The solid line is calculated according to the DLVO theory, while all dashed lines only guide the eye. The Π–h curve without NaCl is the same as the one in Fig.3(a).

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