Hydration force due to the reduced screening of the electrostatic repulsion in few-nanometre-thick films

Peter Kralchevsky*, Krassimir Danov and Elka Basheva

Dept. Chemical Engineering, Faculty of Chemistry, Sofia University, 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria
* e-mail: pk@lcpe.uni-sofia.bg

Numerous experiments show that a strong short-range repulsion exists in thin films formed from aqueous solutions, which was termed hydration repulsion. Unlike the conventional electrostatic double-layer surface force, the hydration repulsion increases with the rise of electrolyte concentration and is an important factor for the stability of liquid films and various dispersions. We investigated this effect with foam films from solutions of 1 mM SDS + 100 mM Electrolyte (LiCl, NaCl and CsCl) by a thin-film-pressure balance. The measured dependences of disjoining pressure versus film thickness exhibit a steep increase when the thickness of the film’s water core becomes smaller than 3.7 nm. This behaviour can be interpreted as a manifestation of the hydration force. Its dependence on the film thickness does not follow a simple exponential law.

Electrostatic disjoining pressure vs. film thickness. At small $h$, all coions are pressed out of the film.

We unsuccessfully tried to interpret the data with different available theoretical models. Eventually, we found that a relatively simple “reduced screening” (RS) model can fit the data. It assumes that at sufficiently small thicknesses all coions are pressed out of the film, so that it contains only counterions dissociated from the ionized surface groups. Under such conditions, the screening of the electric field of the film surfaces weakens, which considerably enhances the electrostatic repulsion between them in comparison with that predicted by the conventional double-layer theory. Such reduced screening of the electric field could exist only in a narrow range of film thicknesses, which practically coincides with the range where the hydration repulsion is observed. It is demonstrated that in combination with a charge-regulation regime, the proposed reduced-screening model of the hydration force can provide a quantitative explanation of the observed strong repulsion at small separations [1].