Effect of ionic correlations on the surface forces in thin liquid films: Influence of multivalent coions and extended theory

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Experimental data for the disjoining pressure of foam films stabilized by anionic surfactant in the presence of 1:1, 1:2, 1:3 and 2:2 electrolytes: NaCl, Na_2SO_4, Na_3Citrate and $MgSO_4$ are reported. The disjoining pressure predicted by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory coincides with the experimental data in the case of 1:1 electrolyte, but it is considerably greater than the measured pressure in all other cases (Figure 1). The theory is extended to account for the effects of ionic correlations and finite ionic radii. Original analytical expressions are derived for the local activity coefficient, electrostatic disjoining pressure and asymptotic screening parameter. With the same parameter of counterion binding, as for 1:1 electrolyte, the curves predicted by the extended theory are in perfect agreement with the experimental data for 1:2, 1:3 electrolytes. In comparison with the DLVO theory, the effect of ionic correlations leads to more effective screening of electrostatic interactions; to lower electric potential and counterion concentrations in the film's midplane that results in lower disjoining pressure, as experimentally observed [1]. The developed theory is applicable to both multivalent coions and multivalent counterions. Its application could remove some discrepancies between theory and experiment observed in studies with liquid films from electrolyte solutions.

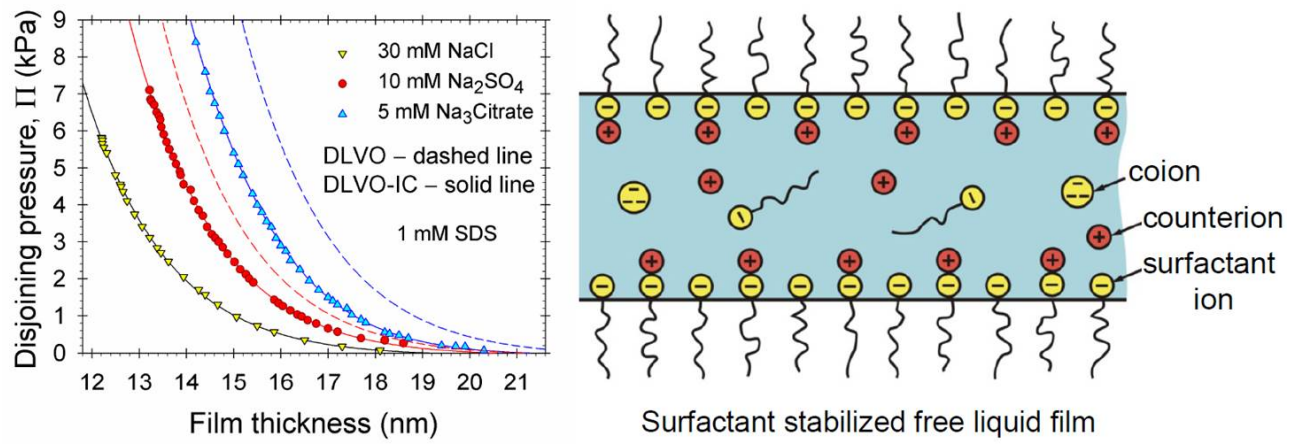

Figure 1. (Left) Dependences of disjoining pressure, Π, on the experimental film thickness measured by thin-film-pressure balance. The points are experimental disjoining pressure isotherms of thin foam films stabilized with 1 mM SDS in the presence of three different salts, NaCl, Na_2SO_4 and Na_3Citrate at the same total ionic strength, I = 31 mM. The dashed and solid lines are drawn using the conventional DLVO theory and the DLVO theory with ionic correlations (DLVO-IC). In the case of NaCl, the predictions of DLVO and DLVO-IC coincide. (Right) Sketch of a foam film, like those studied in our experiments, with surfactant ions, counterions and coions.

[1] K.D. Danov, E.S. Basheva and P.A. Kralchevsky, *Materials,* 2016, **9**, 145.