Aggregation of Colloidal Particles in the Presence of Multivalent Coions: The Inverse Schulze–Hardy Rule

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The classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory predicts that colloidal suspensions are stable at low salt concentrations and are unstable at higher ones[2]. The transition between these two regimes is referred to as the critical coagulation concentration (CCC). For highly charged particles, the DLVO theory suggests $CCC \propto 1/z^6$, where z is the counterion valence. This dependence is called the Schulze-Hardy rule.

In this work, the aggregation behavior of positively charged amidine latex particles and negatively charged sulfate latex in salt solutions containing *multivalent coions* and monovalent counterions was studied by time-resolved light scattering techniques. The results show that the CCC is inversely proportional to the *coion valence*. We argue that an analogous the *inverse Schulze-Hardy rule* can be formulated in this situation, namely $CCC \propto 1/z$. The dependencies of the CCC on the valence predicted by *inverse Schulze-Hardy rule* and the Debye-Hückel theory ($CCC \propto 1/z(z+1)$) are compared with the experimental data (Fig. 1a). We have also carried out DLVO calculations of the CCCs within the Poisson-Boltzmann theory for different charge densities (Fig. 1b)[2]. For high charge densities, the $1/z$ dependence is obtained, while the Debye-Hückel dependence is recovered for low charge densities.

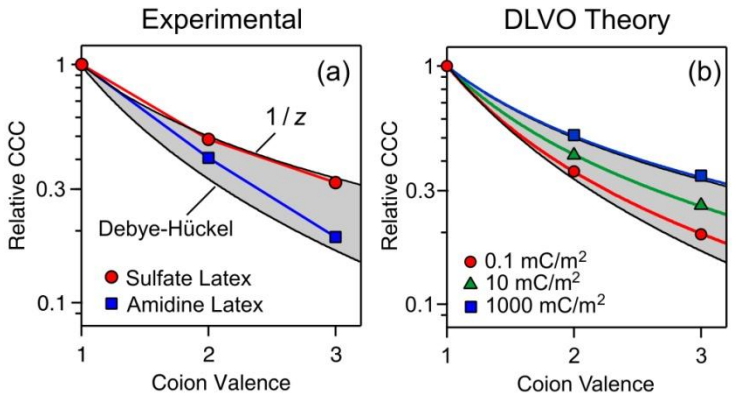

Figure 1 CCC normalized to its value in the monovalent electrolyte versus the valence of the coions in the salt solutions used.

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[2] G. Trefalt, I. Szilagyi and M. Borkovec, *J. Colloid Interf. Sci.,* 2013, ***406***, 111.