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

Tianchi Cao1*, Istvan Szilagyi1, Tamas Oncsik1, Michal Borkovec1, Gregor Trefalt1

1Department of Inorganic and Analytical Chemistry, University of Geneva, Geneva, Switzerland

Tianchi.Cao@unige.ch

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 $\text{CCC} \propto 1/z^6$, 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 $\text{CCC} \propto 1/z$. The dependencies of the CCC on the valence predicted by inverse Schulze-Hardy rule and the Debye-Hückel theory (CCC $\propto 1/ \varepsilon (z+1)$) 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.

Acknowledgements The financial support of the Swiss National Science Foundation and the University of Geneva.