

Multivalent Counterions versus Multivalent Coions: Particle Aggregation and Surface Forces

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Particle aggregation in the presence of multivalent counterions has been studied for a long time. More than a century ago Schulze and Hardy discovered that the coagulation power of a counterion increases dramatically by increasing its valence [1]. This observation was later explained theoretically by Derjaguin, Landau, Verwey, and Overbeek (DLVO) and the derivation of the Schulze-Hardy rule is considered as a triumph of the DLVO theory [2]. In my talk I will revisit this derivation and assess the validity of the assumption put forward in the DLVO theory. Furthermore I will address the issue of the multivalent coions, which were only rarely addressed in the context of surface forces and particle aggregation [3]. Multivalent coions largely affect the electrostatic forces between the charged surfaces and induce a different aggregation behavior as compared to their counterion counterparts. The effect of multivalent coions on the particle aggregation could be explained by the *inverse* Schulze-Hardy rule.

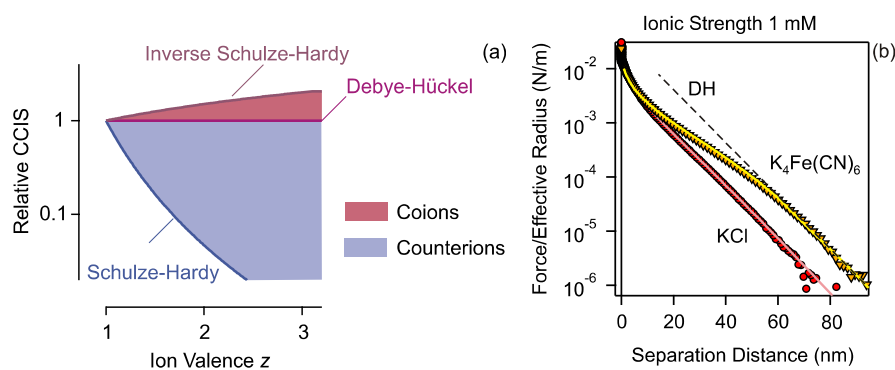


Figure: (a) Aggregation of colloids in the presence of multivalent counterions and coions. (b) Effect of multivalent coions on force between charged silica particles.

[1] Schulze, H. J. *Prakt. Chem.* 1882, **25**, 431–452. Hardy, W. B. *Proc. R. Soc. London* 1899, **66**, 110–125.

[2] Derjaguin, B.; Landau, L. D. *Acta Phys. Chim.* 1941, **14**, 633–662. Verwey, E. J. W.; Overbeek, J. T. G. *Theory of Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

[2] Trefalt et al., *Langmuir*, 2017, **33**, 1695–1704. Cao et al., *Langmuir*, 2015, **31**, 6610–6614. Uzelac et al., *Soft Matter*, 2017, **13**, 5741–5748.