

DLVO Theory and the Lubetkin-Middleton-Ottewill Law of Dissociation of Charged Interfaces

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The DLVO theory has been a “textbook” theory of colloidal stability for over 50 years; it is a summation of repulsive electrostatic forces and attractive van der Waals forces (1). Here, we are concerned with the screened electrostatic forces only. We examine their theoretical foundation in the non-linear Poisson-Boltzmann equation (NLPB), whose inconsistencies are known but hard to clarify; we argue that an electrostatically sound approach is required to make the most of the Poisson-Boltzmann paradigm.

We outline a linear electrostatic model - a “Maxwellian” model - in which charge densities and potentials are linearly related in every differential volume element, as required by the Poisson equation of Maxwellian electrostatics. The Maxwellian linearity leads to a system of contiguous linear Poisson-Boltzmann (PB) equations with free boundaries that demarcate co-ion exclusion regions at high potential surfaces (2, 3). At low potentials this system of Maxwellian PB equations folds into to a single PB equation (the Debye-Hückel model). The exclusion boundaries are not arbitrary but are obtained as free-boundary solutions of the contiguous PB equations. The positions of these boundaries represent “diffuse structure” of ionic distributions near charged surfaces. These boundaries also undergo “Cheshire cat” transitions, *i.e.* appear or disappear from charged surfaces at critical physicochemical conditions. Additional transitions become apparent for interacting charge surfaces.

The Maxwellian model has been applied to data on swelling pressures of montmorillonite clays (4-7). Two fundamental results have emerged and are of some interest. First, the greater dissociation of charged interfaces with increasing bulk ionic concentrations is described by the Lubetkin-Middleton-Ottewill (LMO) law. This law reduces to either 100% dissociated Gouy-Chapman model or to the undissociated Helmholtz model of charged interfaces. The LMO law is an example of “Debye-Hückel inter-ionic phenomena”, when free ion activities are reduced; such reduction leads to changes in ionic equilibria and in rates of ionic reactions. Second, the theory provides a limiting law that predicts very large repulsions as two charged surfaces approach, thereby obviating the need for non-DLVO “hydration” forces (2). Some other results and applications are also briefly discussed (8-11); but the 3-dimensional problem of two (or more) interacting spheres that dissociate according to the LMO law remains unsolved.

References

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