



Poisson–Boltzmann description of interaction forces and aggregation rates involving charged colloidal particles in asymmetric electrolytes

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ABSTRACT

Forces and aggregation rates involving spherical particles are studied numerically within the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) for asymmetric and mixed electrolytes. Thereby, the double layer interactions are treated at the Debye–Hückel (DH) and Poisson–Boltzmann (PB) levels. The DH model is applicable for weakly charged systems, and effects of ion valence enter only implicitly through the ionic strength. The PB model is necessary for more highly charged systems, and depends on the actual ionic composition. One finds that forces in asymmetric electrolytes at fixed ionic strength weaken when the valence of the counterions is increased or when the valence of the coions is decreased. In symmetric electrolytes, the effect of counterions is more important than the one of the coions. For weakly charged systems, the critical coagulation concentration (CCC) decreases with the square of the valence in symmetric electrolytes, while this decrease is weaker in asymmetric ones. With increasing charge density, the dependence of the CCC on the valence becomes stronger, but the classical Schulze–Hardy decrease with the sixth power of the valence is only recovered for unrealistically high charge densities. Mixtures of electrolytes are treated within the same framework, and one observes that already small amounts of multivalent ions affect the system considerably. An empirical mixing rule is proposed to describe the calculated CCCs.

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1. Introduction

The Poisson–Boltzmann (PB) theory represents the cornerstone of our quantitative understanding of interactions between charged surfaces in aqueous solutions [1,2]. This theory is often capable to rationalize experiments with astonishing accuracy [3–12]. For example, directly measured forces across electrolyte solution between mica sheets or involving colloidal particles can be described with PB theory quantitatively, especially at larger distances [3–5]. When the interaction forces obtained from PB theory are added to the omnipresent van der Waals forces, one arrives at the classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) [1,2,13,14]. The DLVO theory is equally capable to describe the transition between repulsive and attractive regime at higher salt levels as well as particle aggregation rates in colloidal suspensions [7–9,11,15]. While PB was mostly used in the presence of monovalent electrolytes [3–10,15], recent findings indicate this theory to be applicable in the presence of multivalent ions as well [10–12].

While the PB model normally relies on a numerical solution of a non-linear differential equation [9,10,16,17], Debye–Hückel (DH) theory often permits analytical solutions due to its linearity

[2,18,19]. However, the DH theory is only valid for sufficiently low potentials, and in this regime it is precisely equivalent to PB theory. However, the range of validity of DH theory depends on type of ions, and its range of validity is smaller in the presence of multivalent ions than for monovalent ones. Nevertheless, DH theory may be sufficiently accurate to describe the relevant interactions properly, especially at larger distances and when combined with the notion of the effective (or renormalized) potential or charge [20,21].

Double layer forces deduced from PB theory may strongly depend on the boundary conditions, especially at shorter distances [2,18,19]. Normally, the constant charge (CC) and constant potential (CP) boundary conditions are considered. However, these are only two special cases. Upon approach, the surfaces will normally regulate their charge and the nature of this regulation strongly influences forces at shorter distances [18,19,22]. This regulation originates from shifts in the adsorption equilibrium of charged ions upon approach due to the deformation of the diffuse layer. While a detailed treatment of this phenomenon requires a consideration of the adsorption equilibrium of all the relevant ions, a simpler description is possible within the constant regulation (CR) approximation [23]. This approximation stipulates that charge regulation effects can be considered to first order in terms of a constant inner capacitance of the adsorbed layer. While this approach is only

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appropriate at larger distances, it provides a simple framework to quantify regulation effects in actual systems. Charge regulation effects were equally suggested to modify the shift of the critical coagulation concentration (CCC) with the valence of the counterions [24–26].

Due to their relative simplicity, DH and PB descriptions have been used to address a wide range of electrostatic phenomena. Many researchers have discussed the effect of surface charge heterogeneities [27–30]. The situation can be treated analytically on the DH level on a regular lattice, and it was found that such charge heterogeneities can induce additional attractive forces [27,28]. The range of these additional interactions is given by the lattice spacing at low salt levels, but this interaction becomes screened at higher salt levels. These effects were also treated numerically within the surface element approximation [29,30]. Three-body forces represent another aspect studied within the PB approximation [17,31,32]. While DH theory predicts pair-wise additive forces due to its linearity, one obtains three-body forces on the PB level. These forces turn out to be attractive, and their importance was confirmed experimentally [31,32].

The classical PB model neglects finite ion size and relies on a mean-field description of the electrolyte solution [2,33–36]. Finite-size effects are commonly approximated by introducing a Stern layer or by treating the finite size of the ions in a self-consistent fashion [37–39]. Detailed analysis reveals that the mean-field approximation inherent to the PB model may fail in the case of strong electrostatic coupling, which becomes important for highly charged surfaces, multivalent ions, or non-aqueous electrolytes of low dielectric constant [25,26,33–36]. These findings triggered renewed interest in adsorption processes involving multivalent ions and how their presence influences forces between colloidal particles [36,40,41].

In spite of these shortcomings, PB theory is expected to be applicable at larger distances from the surface, where high electrical potentials and crowding effects have decayed away. In this case, however, the relevant parameters entering the PB theory, such as the surface potential, surface charge, or regulation capacitance, refer to the entire surface layer sandwiched between the plane of origin of the diffuse layer and the actual interface. In this situation, one also refers to effective (or renormalized) charge or diffuse layer potential. The experimental determination of such effective potentials seems relatively straightforward with electrokinetic techniques [2], scattering experiments [20], or direct force measurements [4,5]. Direct force and aggregation measurements suggest that PB theory represents a good approximation down to distances of few nm in the presence of monovalent electrolytes [3–10]. Recently, it was even reported that PB theory could be applicable in the presence of multivalent ions at larger separation distances [10–12]. On the theoretical side, however, it seems not quite clear at which distances ion correlations and crowding effects can be neglected and the PB model becomes valid. Especially, it has not yet been established how this region of validity depends on the valence of the ions present. The PB theory might have therefore a much wider range of applicability than expected so far. This fact would substantially simplify the analysis of interaction forces in such systems at larger distances. This possibility would be rather intriguing, since accurate predictions based on current theories including ion correlations normally rely on time-consuming computer simulations [25,26,35,36,42].

In the present article, we therefore analyze forces and aggregation rates calculated within the PB model in the presence of asymmetric and mixed electrolytes, especially considering multivalent ions. The available literature hardly touches upon this topic [43–45]. We discuss the effect of the non-linearity inherent to the PB description and will demonstrate that the DH theory remains good approximation in many situations. Moreover, we analyze the

dependence of the CCC on the valence of the counterion z . We find that the popular Schulze–Hardy dependence of z^{-6} can be only recovered for surfaces with unrealistically high charge densities, and that rather the weaker z^{-2} dependence predicted by DH theory should be expected. Since PB theory is likely to be also applicable in the presence of multivalent ions, it is essential to analyze the predicted dependencies on the forces and aggregation rates in detail.

2. Modeling

The interactions are modeled with the PB and DH models in the symmetric plate–plate geometry. These results are transformed to the sphere–sphere geometry by means of the Derjaguin approximation, in order to obtain experimentally accessible force profiles and aggregation rates.

2.1. Poisson–Boltzmann theory

Let us consider an electrolyte solution between two charged plates containing different types of ions of concentration c_i and charge z_i , expressed in units of the elementary charge q . The electric potential $\psi(x)$ depends on the position x , whose origin is taken at the mid-plane, and satisfies the PB equation [1,2]

$$\frac{d^2\psi}{dx^2} = -\frac{q}{\varepsilon_0\varepsilon} \sum_i z_i c_i e^{-z_i\beta q\psi} \quad (1)$$

where the sum runs over all types of ions i , and ε_0 is the dielectric permittivity of vacuum, ε the dielectric constant, and $\beta = 1/(k_B T)$ the inverse thermal energy. In the latter equation T is the absolute temperature and k_B is the Boltzmann constant.

For large plate separations Eq. (1) can be integrated once, and one obtains for any of the two plates their surface charge density

$$\sigma = \pm \left[2k_B T \varepsilon_0 \varepsilon \sum_i c_i (e^{-z_i\beta q\psi_D} - 1) \right]^{1/2} \quad (2)$$

where ψ_D is the surface (or diffuse layer) potential for the isolated plane and \pm refers to positive and negative surface potentials. The differential diffuse layer capacitance of the isolated layer can be obtained from the derivative

$$C_D = \frac{\partial\sigma}{\partial\psi_D} = \pm \left(\frac{q^2 \varepsilon_0 \varepsilon}{2k_B T} \right)^{1/2} \frac{\sum_i z_i c_i (e^{-z_i\beta q\psi_D} - 1)}{\left[\sum_i c_i (e^{-z_i\beta q\psi_D} - 1) \right]^{1/2}} \quad (3)$$

where \pm has the same meaning as in Eq. (2). Within the constant regulation (CR) approximation, the solution of the PB equation in the plate–plate geometry must be found subject to the boundary conditions [23]

$$\pm \varepsilon_0 \varepsilon \frac{d\psi}{dx} \Big|_{x=\pm h/2} = \sigma - C_1 [\psi(\pm h/2) - \psi_D] \quad (4)$$

where the plates are situated at $x = \pm h/2$ and C_1 is the inner layer capacitance. The inner capacitance is normally replaced by the regulation parameter defined as

$$p = \frac{C_D}{C_D + C_1} \quad (5)$$

One obtains constant charge (CC) boundary conditions for $p = 1$ and constant potential (CP) boundary conditions for $p = 0$. The regulation parameter may become negative, but this situation is probably not too important in practice [22].

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