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Specific ion effects: Interaction between nanoparticles in electrolyte solutions

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Abstract

Dependence of colloidal interactions on salt identity, observed frequently in experiments, can be accounted for once ion specific non-electrostatic forces are included in the theory. Ability to predict the effect of added salt on the phase diagram of colloid dispersions is essential for the design of processes involving nanocolloids. The Ornstein–Zernike equation with hypernetted chain closure approximation provides a viable first estimate for the potential of mean force between ionized nanoparticles like alumina aggregates in aqueous electrolytes subject to dispersion interactions with hydrated simple ions. Calculated potentials of mean force enable the prediction of osmotic second virial coefficients and phase diagrams showing a dramatic dependence on ion type. The choice of salt therefore provides an efficient, non-intrusive way to tune the phase behavior of nanoparticle dispersions.

Keywords: Hofmeister effect; Polarizability; Ionic dispersion potentials; Nanoparticles; OZ–HNC integral equation; Phase diagram

1. Introduction

Control of the interaction between nanoparticles in aqueous electrolyte solution is important for applications as diverse as process design in nanotechnology, selective minerals flotation and crystallization of proteins. It has been shown that previously ignored dispersion forces between electrolyte ions and dispersed nanoparticles result in strong ion-specific effects on the potentials of mean force between globular nanoparticles in electrolyte solutions. This opens up new possibilities to exploit salt identity to manipulate nanoparticle interactions. An understanding of how the potential of mean force behaves in different salt solutions is essential for control of the phase behavior of nanoparticle solutions. We here describe and apply an integral-equation framework for the calculation of potentials of mean force between ionic nanocolloids. Combined with first order perturbation theory, our method allows the prediction of osmotic second virial coefficients and phase diagrams. Our approach is illustrated by model calculations in a system roughly mimicking the industrially important case of alumina nanoparticle solutions.

According to classical DLVO theory [1], as well as more complicated theories [2–4] that rely on either an electrostatic primitive model representation [5], or decorations that use molecular solvent models, the dominating ionic property that influences the interaction between a pair of nanoparticles in salt solution is the ionic charge. All monovalent salts should have very similar effects, modulated only weakly by a hypothetical hydrated ion size. This is not what is seen experimentally. The choice of the ion pair of the electrolyte plays a significant role [6]. As demonstrated in a number of studies [7–9], the main reason for this failure of DLVO theory is the neglect of non-electrostatic (NES) dispersion forces between the ions and colloidal particles.

In the present study, we augment the standard charged-sphere model of colloidal solutions by including the missing

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dispersion interactions between simple ions and nano-sized colloidal solutes. As shown earlier [9], this generalization can be implemented within the McMillan–Mayer approximation [10], where we treat the solvent as a uniform medium whose presence is reflected only in effective solute–solute potentials. Due to the lack of accurate analytical approximations for highly charged macroion solutions, quantitative estimates of protein interactions required the use of simulation techniques [9]. The weakly charged nanoparticles we study here, however, are amenable to accurate integral-equation description of inter-particle correlations including potential of mean force between nanoparticles. This circumstance allows relatively fast yet accurate calculations on low-end desktop computers, a critical advantage for engineering applications. The regime where HNC/Ornstein–Zernike equations are quantitatively reliable has been established through comparisons with computer simulations and small angle neutron scattering data [11,12]. This assessment is not altered by the presence of short-ranged specific forces since the limitations of the theory are related primarily to the long-ranged Coulombic interactions [4]. As the favorable regime includes colloid charges and sizes pertinent to the present study, we are able to apply an accurate analytic formalism to estimate the phase diagram behavior of a colloidal dispersion subject to ion-specific interactions. In view of modest computational requirements and well established routes for estimating ion/colloid van der Waals interactions [9], our approach should be of value in the design of engineering processes involving saline dispersions of nanoparticles.

2. Model and methods

2.1. Specifications of the model

Colloidal dispersions are modeled as a mixture of spherical nanoparticles of diameter σ_m and charge q_m, and monovalent counter- and co-ions of diameter σ_i and charge $q_i = \pm e_o$. Solute particles are dispersed in a continuum solvent medium of permittivity $\varepsilon(T)$. In selecting a plausible prototypical system, we choose model parameters that roughly correspond to a dispersion of alumina nanoparticles in aqueous solutions of NaCl or NaI, with $\sigma_m = 2.0$ nm, $\sigma_i = 0.4$ nm, $q_m = 4e_o$, and ε (298 K) = 78.5 [9]. We emphasize, however, that we use our hypothetical model to provide a more general estimate of the inclusion of dispersion-forces on predicted phase behavior of nanocolloids. To study one effect at a time, the model does not incorporate all complex features of real alumina dispersions [13–15]. An important simplification is the use of fixed nanopoarticle charge. This constraint precludes studies of pH and other conditions, demonstrated [13,14] to represent essential ingredients in quantitative thermodynamic predictions for alumina solutions.

In analogy with earlier integral-equation studies of simple electrolytes [16,17], we augment Coulombic and hard-core potentials characteristic of the primitive model [5] by short ranged ion–macroion interactions. In view of the inequality $\sigma_m \gg \sigma_i$, ion–colloid dispersion potentials are ascribed the form $B_{mi}/[r-(\sigma_m/2)]^3$, where r is the center-to-center distance and B_{mi} the ionic dispersion coefficient specific for each hydrated ion species. We used the strategy described in [9] to obtain the B_{mi}-values of -8.5×10^{-51} J m^3 for Na$^+$, -6.2×10^{-50} J m^3 for Cl$^-$ and -9.9×10^{-50} J m^3 for I$^-$. These potentials subsume all many body interactions in Lifshitz theory in ultraviolet and visible correlations. The variations in strength of ion–particle interactions that include many body dipole-induced dipole and permanent dipole–dipole interactions are reflected in the different B-values. As our integral equation calculations pertain to highly diluted macroion solutions, for the macroion–macroion pair, only electrostatic and hard-sphere repulsion interactions are taken into account in the OZ–HNC calculations. The *exclusion* of the Hamaker term in Fig. 1 shows more clearly the salt-dependent contribution to the potential of mean force.

Dispersion forces also affect the interactions between electrolyte ions as demonstrated in [17] concerned with colloid-free salt solutions. Our calculations with all van der Waals ion–ion terms included, however, show that, at the conditions of the present study, ion–ion dispersion potentials have no significant influence on the inter-colloidal interaction.

2.2. Analysis

Potentials of mean force between dilute nanoparticles are calculated by the Ornstein–Zernike equation with hypernetted chain closure approximation (OZ–HNC) [3,4,16]. Potentials of mean force (augmented by the direct Hamaker potential) are then used to determine osmotic second virial coefficients and phase diagrams. In calculations of the phase diagrams we rely on a first order perturbation theory, recently described by Tavares and Prausnitz [18].

According to the OZ–HNC approximation, spatial correlation functions for cation–macroion, anion–macroion and macroion–macroion pairs are determined through a solution of multicomponent Ornstein–Zernike equations [10] combined

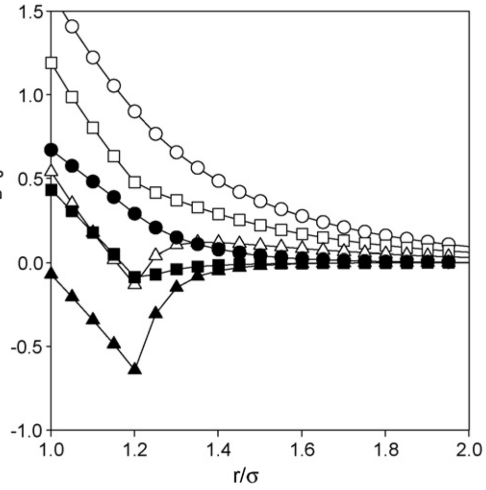

Fig. 1. Normalized interaction potential between aluminium oxide nanoparticles obtained from OZ–HNC as a function of normalized distance. The curves correspond to 0.1 M (open symbols) and 0.5 M (filled symbols) of non-polarizable salt (circles), NaCl (squares) and NaI (triangles). Here T_0 is 298 K.