A Four-Component Model for Small Colloidal Particles in an Aqueous Electrolyte

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Small colloids in a uni-univalent aqueous electrolyte are modeled by a four-component solvent primitive model. The symmetric Poisson−Boltzmann theory is used to analyze the system and to calculate the second virial coefficient B_2 of very dilute particle suspensions for varying solute and solvent concentrations. The results are compared with some experimental results on B_2 of the silicotungstate anion suspension in an alkali halide solution.

Introduction

Theoretical investigations of colloidal systems are usually based on the ideas developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO).[1,2] These authors used an effective colloid−colloid pair potential consisting of an attractive van der Waals term and a repulsive electrostatic term. This potential model is a one-component model in which the influences of the surrounding ions and solvent are essentially subsumed into the electrostatic term. Improvements to the one-component model can be made by incorporating terms such as those which account for the "depletion effect" due to solvent size.[3−5] One-component potentials are very useful, as they can be directly used in integral equation techniques.

Any fundamental advance in colloid theory must come from an adequate treatment of all the particles in the solution. Some work in this direction has taken place in which integral equations[6,7] and symmetrical Poisson−Boltzmann (SPB) and modified Poisson−Boltzmann (MPB) theories[8] have been applied to two- or three-component systems.[9−13] A study has also been made of a four-component system.[14] Solutions involving these models have demonstrated that under certain conditions an attraction can occur between like-charged species. In the

three-component model, one species can be neutral[15−17] and regarded as modeling particles such as nonionic polymers or proteins. An alternative interpretation is to regard the neutral component as modeling the solvent so that the steric effects of the solvent can be investigated. When interpreted in this light the model is known as the solvent primitive model (SPM). A problem with the SPM is that the status of the model relative to the Born−Oppenheimer model is unknown. To apply the SPM to colloidal particles in a single aqueous electrolyte requires treating four molecular species simultaneously. Such a model is difficult to treat using integral equation techniques as they require the simultaneous determination of 10 radial distribution functions.

We consider here the application of the SPB theory to the four-component SPM. Given the radial distribution functions for the underlying discharged hard sphere system, the SPB (or MPB) theory only requires the solution of four simultaneous equations for the mean electrostatic potentials about the four species. Earlier work for three species[13,15,17] implies that we expect the SPB to give reasonable results for a 1:1 electrolyte with not too large a size variation. It thus seems probable that the theory can be applied to analyze colloidal systems which have nanosized particles. In this Letter we calculate the second virial coefficient B_2, for very dilute particle suspensions, which plays a key role in monitoring the attractive interaction between colloid particles. Some recent experimental results for B_2 of the silicotungstate colloid suspension in some alkali halide solutions are then interpreted.

Model

The SPM is a mixture of charged and uncharged hard spheres moving in a dielectric continuum of relative permittivity ϵ_r. For this model the pair interaction $u_{ij}(r)$ between two molecules i and j a distance r apart is

$$u_{ij}(r) = \begin{cases} \infty & r < a_{ij} \\ z_i z_j \, e^2/4\pi\epsilon_0\epsilon_r r & r > a_{ij} \end{cases} \quad (1)$$

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Here z_s is the valence of species s, e_0 the charge on a proton, and $a_{ij} = a_i + a_j$ where a_s is the radius of species s. When s is the neutral species, $z_s = 0$.

The mean electrostatic potential ψ_i about species i satisfies Poisson's equation

$$\nabla^2 \psi_i = -(1/\epsilon_0 \epsilon_r) \sum_s z_s e_0 n_s g_{is}(r) \qquad (2)$$

where $g_{is}(r)$ is the radial distribution function for i and s, n_s is the number density of species s, and the sum is over the species.

In the SPB theory[8]

$$g_{is}(r) = g_{is}{}^0 \exp\{-(e_0/2kT)(z_i[\psi_s + \psi_s{}^0] + z_s[\psi_i + \psi_i{}^0])\} \qquad (3)$$

where $g_{is}{}^0 = g_{is}(z_i = z_s = 0)$, $\psi_s{}^0 = \psi_s(z_s = 0)$, k is Boltzmann's constant, and T is the absolute temperature. The radial distribution functions $g_{is}{}^0$ are approximated by the Percus–Yevick uncharged hard sphere radial distribution functions for mixtures with the Verlet–Weis correction.[7]

Calculations were performed for those values of the parameters which approximated to the experimental values of Zamora and Zukoski[18] on the second virial coefficient B_2 of the silicotungstate anion under varying concentrations of added electrolyte. The coefficient B_2 is given by

$$B_2 = -2\pi \int_0^\infty r^2(g_{cc} - 1)\, dr \qquad (4)$$

where g_{cc} is the colloid–colloid pair distribution function at infinite colloid dilution. The macroion radius and valence were taken to be 5.5 Å and -4, respectively, the neutral species radius $a_N = 1.5$ or 1.8 Å, which cover that of water, and the electrolyte to be uni-univalent with cation and anion radii $a_i = 1.8$ Å, $\epsilon_r = 78.5$, and $T = 298.15$ K. Some calculations were also carried out for two sets of differing ion sizes. Various values of the electrolyte concentration and neutral species were considered, with the limiting value of the macroion concentration being zero for the calculation of B_2.

Results and Discussion

The set of four coupled equations for the mean electrostatic potentials was solved by a previously developed quasi-linearization procedure. This enabled us to investigate the pair distribution function g_{cc}, and hence B_2, for varying neutral species concentration c_N and electrolyte concentration c. The key ingredient of the SPM is the neutral species which allows an estimate to be made of the steric effect of the solvent molecules. Figure 1a shows the influence on g_{cc} of the variation of c_N at $c = 1$ M when $a_N = 1.5$ Å. When $c_N = 0$, which corresponds to a three-component primitive model (PM), the colloid–colloid interaction is purely repulsive. As c_N increases from zero, the exclusion volume effect of the solvent molecules increases in importance, giving rise to structure in g_{cc} and predicting attraction at small separations.

In the theory the structure comes predominantly from the uncharged hard sphere radial distribution functions $g_{ij}{}^0$. At the higher values of c_N the PY uncharged distribution function $g_{cc}{}^0$ becomes negative leading to unphysical values of g_{cc}. The critical values of c_N at which this occurs for the parameters considered here are given in Table 1.

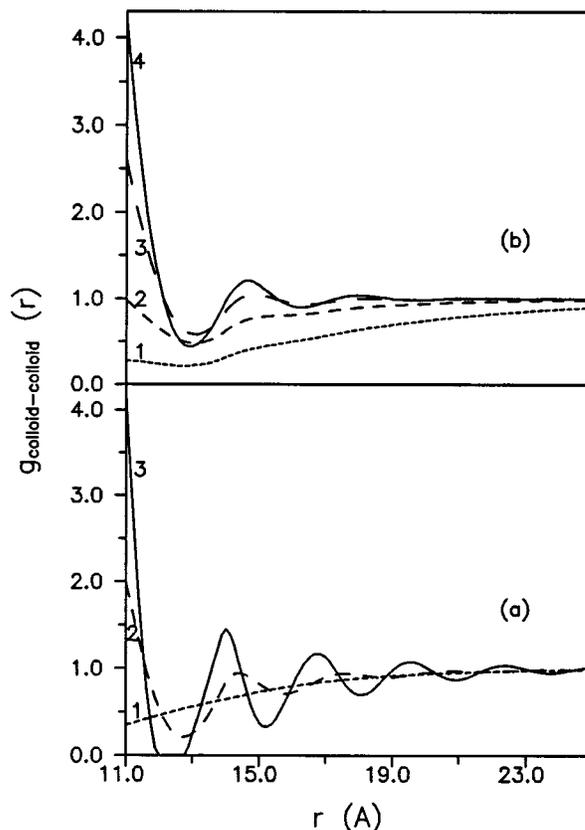(18) Zamora, P. C.; Zukoski, C. F. *Langmuir* **1996**, *12*, 3541.

Figure 1. Colloid–colloid radial distribution function at infinite colloid dilution for 1:1 electrolytes with ion radii $a_i = 1.8$ Å, $a_N = 1.5$ Å, and colloid radius 5.5 Å: (a) $c = 1$ M with curves 1, 2, and 3 denoting $c_N = 0$, 35, and 50 M, respectively, with corresponding total packing fraction $\eta_T = 0.029$, 0.327, and 0.455; (b) $c_N = 20$ M with curves 1, 2, 3, and 4 denoting $c = 0.3$, 1, 3, and 5 M, respectively.

Table 1. The Values of Electrolyte Concentration c and Neutral Species Concentration c_N at Which the PY $g_{cc}{}^0$ Become Unphysical[a]

c (M)	c_N	
	(a)	(b)
0.3	45	28
1.0	43	27
3.0	37	23
4.0	33	21
5.0	30	19

[a] Column a corresponds to Figure 2a and column b to Figure 2b. For (a) $\eta_T \sim 0.40$ and for (b) $\eta_T \sim 0.43$.

When the ions and solvent have the same radius of 1.8 Å, this happens for the total packing fraction $\eta_T \sim 0.43$, and for $\eta_T \sim 0.40$ when a_N is reduced to 1.5 Å. These values for the total packing fraction are to be compared with the PY results for a simple hard-sphere fluid which predicts a fluid phase for $0.49 < \eta < 0.62$ and becomes unphysical for $\eta > 0.62$. The addition of the colloids, even at infinite colloidal dilution, means that for the situation when all the remaining molecules are of comparable size, the osmotic depletion effect has a profound effect on the colloidal distribution. Some calculations were also performed above these critical values of c_N. When this occurs the negative values are smoothed to very small positive values so that g_{cc} remains physical, see Figure 1a for $c = 50$ M in the neighborhood of $r = 12$ Å. Unfortunately there is at present no other satisfactory theory for a four-species system of uncharged hard spheres.[19] This is highlighted by the on going work on the phase behavior of asymmetric
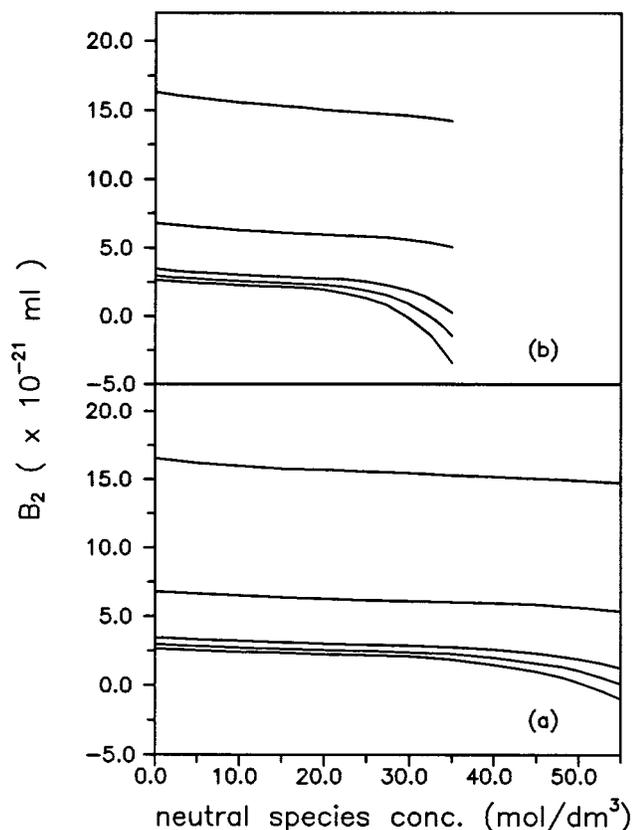
Figure 2. The second virial coefficient B_2 at five electrolyte concentrations 0.3, 1, 3, 4, and 5 M for varying neutral species concentration c_N: (a) with ion radii $a_i = 1.8$ Å and $a_N = 1.5$ Å; (b) for $a_i = a_N = 1.8$ Å. In both figures the curves from the top to the bottom are for $c = 0.3$, 1, 3, 4, and 5 M, respectively.

Table 2. [a]

	B_2 (nm³)			c_N (M)		
c (M)	SPB	MPB	Li₄STA	(i)	(ii)	(iii)
0.3	16.5	14.1	10.3	45.2*	42.8*	45.2*
1.0	6.79	6.10	6.1	21.6	24.6	14.7
3.0	3.43	3.55	1.3	31.2	27.9	32.2
4.0	2.93	3.15	−0.3	33.0	26.8	32.4
5.0	2.61	2.87	−2.0	34.0	25.2	32.4

[a] Columns 2−4 are the B_2 values for the SPB, MPB, and experimental values for Li₄STA[18] at five electrolyte concentrations, c. The error in the experimental results ∼±0.2 nm³. The SPB and MPB results are for the three-component PM with ion radii 1.8 Å and colloid radius 5.5 Å. The final three columns correspond to the four-component model and report the values of c_N at which the experimental values of Li₄STA are obtained for $a_N = 1.8$ Å and different values of cation a_+ and anion a_- radii: (i) $a_- = 0.7$ Å, $a_+ = 1.8$ Å; (ii) $a_- = 1.8$ Å, $a_+ = 2.4$ Å; (iii) $a_- = a_+ = 1.8$ Å. * indicates $\eta_T > 0.6$ for agreement.

binary hard-sphere mixtures.[20−22] Figure 1b shows how the structure of g_{cc} changes with electrolyte concentration at fixed c_N. For low electrolyte concentration the effective colloid−colloid pair potential is repulsive, eventually becoming attractive at contact at the higher electrolyte concentrations.

The experimental results of Zamora and Zukoski on B_2 show that as the electrolyte concentration is increased, its value decreases. In particular at high electrolyte concentrations B_2 can become negative, which is indicative of phase behavior. In Figure 2 results for B_2 are given for two different values of a_N at five electrolyte concentrations and varying neutral species concentration. When $c_N = 0$ the resultant three-component PM yields the corresponding SPB and MPB values given in Table 2. For this PM the values of B_2 decrease as the electrolyte concentration increases, with the MPB value being less than the SPB value at the lowest concentration $c = 0.3$ M, the remaining results being comparable, but always positive. The introduction of a van der Waals interaction into this three-component model reduces the SPB and MPB values of B_2, but negative values still cannot be achieved. On c_N being increased from zero, the SPB value of B_2 slowly decreases. As c_N approaches the critical value at which the PY g_{cc}^0 become unphysical, the rate of change increases with negative B_2 only being achieved for c_N above the critical value. Increasing a_N increases the total packing fraction

at fixed electrolyte concentration and, hence, reduces the corresponding critical value of c_N; see Figure 2. Agreement with experiment can be made by an appropriate choice of c_N and ion radii for fixed c and a_N; see Table 2. Any interpretation associated with these values must be treated with caution due to the unphysical PY g_{cc}^0. At the lowest electrolyte concentration of 0.3 M the theory is inapplicable and a theory which treats fluctuation terms, such as the MPB theory, should be used. We would expect a more accurate theory to give both acceptable results at low c and predict a negative B_2 at high c. The variation of B_2 with T was also calculated and, for fixed electrolyte and solvent concentration, found to increase with increasing temperature consistent with experimental trends.[23]

A serious drawback to a confident explanation of the experimental results is the unphysical behavior which occurs in g_{cc}. This is not surprising due to the lack of knowledge of the phase behavior of a four-component system of uncharged hard spheres. Such knowledge is crucial in amplifying the osmotic depletion effects. A second restriction is the use of the SPB theory, which not only approximates the exclusion volume term through the PY uncharged distribution functions but also neglects the so-called fluctuation term. The fluctuation term is approximately catered for in the MPB theory and is important at the lower electrolyte concentrations as it reduces the diffuse layer around a colloidal particle, leading to a reduction in B_2. See Table 2 for the results for the three-component PM. At the higher electrolyte concentrations the fluctuation term needs to be more accurately treated in the present MPB theory to cater for size asymmetry. The final major shortcoming in the theory is the SPM. Clearly this is an inconsistent model as the macroscopic dielectric constant ϵ_r should arise naturally from an appropriate treatment of the solvent molecules, not be introduced via the pair potentials. The value of the SPM is that it concentrates on the steric effects of the solvent and enables an estimate to be made of these terms. The SPM indicates that the steric effect of the solvent molecules is a key factor in determining the behavior of small colloidal particles at high electrolyte concentrations. At low electrolyte concentrations, Zamora and Zukoski found that the classical DLVO theory provided a reasonable explanation of their experimental work, but it could not explain the attraction found at the higher electrolyte concentrations. Multicomponent models provide a natural framework for an overall understanding of such colloidal systems. The present SPM is a very crude model for

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colloidal particles in an aqueous electrolyte, but we would hope that it is a precursor to those models which treat the solvent more realistictly.

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