Macroion-macroion correlations in the presence of divalent counterions. Effects of a simple electrolyte

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Abstract

The Monte Carlo and integral equation results are presented for a primitive model of a micellar solution. The macroions and small ions are modeled as charged hard spheres embedded in a continuous dielectric. The ratio of diameters of the macroions and small ions (counterions and co-ions) is 3.0 nm : 0.4 nm. The macroions are charged with 20 negative charges, the co-ions have one negative charge, and the counterions may carry one or two positive charges. In a previous study of solutions containing macroions and counterions (B. Hribar and V. Vlachy, *J. Phys. Chem. B*, **1997**, *101*, 3457-3459) it was found that in solutions with monovalent counterions (-20:+1) the macroions were distributed at large distances from each other, while in solutions with divalent counterions (-20:+2) the macroions shared the layer of counterions. In the present paper the effects of addition of a simple electrolyte to these solutions are explored. For systems with monovalent counterions, addition of a low-molecular weight electrolyte causes the macroions to approach each other; the first peak of the pair-distribution function is shifted toward smaller distances. On the other hand, the solutions with divalent counterions seem to be less affected by addition of a simple electrolyte. The results for the excess internal energy, and osmotic coefficient for two different macroion concentrations are presented in addition to the structural information.

Introduction

Several experimental [1, 2, 3, 4, 5], and theoretical studies (for a comprehensive review see [6, 7]) published in the last decade are clearly inconsistent with the

classical DLVO theory of colloid stability [8]. The latter classical theory is based on the assumption that an overlap of the electrical double-layers always leads to repulsive interaction, and that short-range van der Waals forces are responsible for attraction and consequently for coagulation of colloids and micelles [8]. Recent computer simulations of asymmetric electrolytes with an asymmetry in diameter of 3.0 nm : 0.4 nm and in charge of -20 : z_c, where z_c is +1 or +2 revealed [9] that the charge of the counterions z_c determines the distribution of macroions in solution. In particular, in solutions with divalent counterions the macroins are distributed less uniformly than in solutions with monovalent counterions. For a 0.01 M solution of macroions, the probability of finding a neighbour macroion, as determined by the pair distribution function (pdf), is at a distance of 3.9 nm, while the peak of the pdf in a solution where the monovalent ions neutralize the macroions is about 5.4 nm for this concentration [9]. In solutions with trivalent counterions the effect is even stronger; the macroions form clusters which are relatively stable against dilution [10, 11]. This unexpected result, which is in disagreement with the classical DLVO theory, was confirmed by other groups using similar theoretical tools [12, 13, 14].

This work is part of an ongoing project of applying theoretical methods to understand the properties of highly asymmetric electrolytes. In a previous paper [15] we studied a system containing macroions and a mixture of mono- and divalent counterions. We showed that the structure of the solution gradually changes on replacing monovalent counterions with divalent ones. In solutions with divalent counterions the spatial distribution of macroins is much less uniform than in corresponding solutions neutralized by monovalent counterions, and the well known cell model is not a good approximation for these systems [16]. In micellar solutions, as also in colloidal suspensions, the interactions between macroions are substantially modified by addition of a simple electrolyte. An addition of a low molecular weight electrolyte normally destabilizes the solution (or suspension) by screening the repulsive interaction between the macroions. The main goal of the present work is to investigate how the addition of a simple electrolyte affects the strong correlations between the divalent counterions, responsible for the non-uniform distribution of macroions in these solutions. As in several previous studies [9, 10, 11, 15, 16] the Monte Carlo method and the hypernetted-chain integral equation theory were used to calculate ionic distributions and thermodynamic parameters for the model solution.

The model and methods

The system considered here is composed of macroions (m), counterions (c) and co-ions (k). These ionic species are represented by charged hard spheres of different diameters σ_i: i) macroions carry 20 negative charges (z_m = -20, σ_m = 3.0 nm), ii) the counterions have charge z_c = +1 or z_c = +2, and ii) for co-ions z_k = -1. The counterions and co-ions are assumed to be of equal size $\sigma_k = \sigma_c$ = 0.4 nm. The particles representing ions are embedded in a continuous dielectric with permittivity ε. The pair interaction potential for two particles separated by distance r_{ij} is defined by

$$u_{ij}(r_{ij}) = \begin{cases} -\frac{z_i z_j e^2}{4\pi\varepsilon\varepsilon_o r_{ij}} & r_{ij} \geq \sigma_{ij} \\ \infty & r_{ij} < \sigma_{ij} \end{cases} , \tag{1}$$

where e is the proton charge and $\sigma_{ij} = (\sigma_i + \sigma_i)/2$. Monte Carlo simulations were performed at constant volume and temperature with 64 (or in some cases 128) macroions in the system, using the standard Metropolis algorithm [17]. From 50 to 70 million configurations, after an equilibration run of 10 million configurations, were needed to obtain reliable statistics. To avoid effects due to the finite size of the system the Ewald summation method [18] was used. The numerical error in our simulation is estimated to be about 2% in osmotic coefficients and below 1% for the excess internal energies.

The hypernetted-chain (HNC) integral equation theory consists of two equations. One is the Ornstein-Zernike equation, which correlates the total correlation function, $h_{ij}(r) = g_{ij}(r) - 1$, and the direct correlation function, $c_{ij}(r)$ [17]

$$h_{ij}(12) = c_{ij}(12) + \sum_l \int c_{il}(13)\rho_l h_{lj}(32)d(3), \tag{2}$$

where (3) is a short-hand notation for the position $\mathbf{r}_3$, and ρ_l is the number density of the component l. The second equation is given by [17]

$$c_{ij}(12) = h_{ij}(12) - \ln\left[1 + h_{ij}(12)\right] - \beta u_{ij}(12) + B_{ij}(12). \tag{3}$$

As usual $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T absolute temperature. The HNC approximation sets the unknown bridge function $B_{ij}(r)$ to zero for all distances r. A necessary first step toward numerical solution of the HNC equation for ionic systems is the renormalization procedure. For three-dimensional ionic fluids, this procedure is well known; for more details about the numerical procedure see, for example, [19]. The HNC theory has been thoroughly tested against the 'exact' Monte Carlo data for highly asymmetric electrolytes [19, 20]; the conclusion

is that it represents a viable alternative to time consuming computer simulations. Unfortunately, there is a range of parameters (dilute solutions and/or highly charged macroions) where the HNC theory fails to give convergent results [20, 21]. For this reason we have limited our HNC calculations to $c_m = 0.02$ M solution of macroions. The temperature was $T = 298$ K and $\varepsilon = 78.54$ for all calculations.

Results and discussion

We consider first the results for the macroion-macroion pair distribution function (pdf) $g_{mm}(r)$: The results for solutions with monovalent counterions are presented in Figure 1 and the results for divalent counterions are shown in Figure 2. In the first case we consider a mixture of i) -20:+1 and -1:+1 electrolytes, and in the second case we have a mixture of ii) -20:+2 and -1:+2 electrolytes. In both cases the concentrations of macroions was $c_m = 0.02$ M, while the concentration of co-ions in the added electrolyte was $c_k = 0.80$ M. Two conclusions can be made on the basis of these figures.
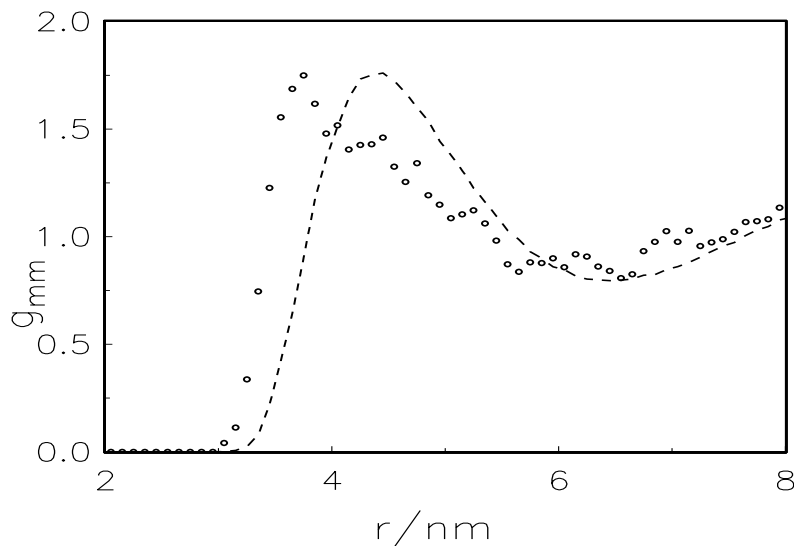

Figure 1: Monte Carlo results for macroion-macroion pdf at $c_m = 0.02$ M in solutions with monovalent counterions. The results for $c_k = 0$ (no added electrolyte) are presented by a dashed line and symbols denote the results for the mixture ($c_k = 0.80$ M).

First, in the mixture with monovalent counterions the macroions distribute themselves at considerably larger distances than in the solution containing divalent coun-
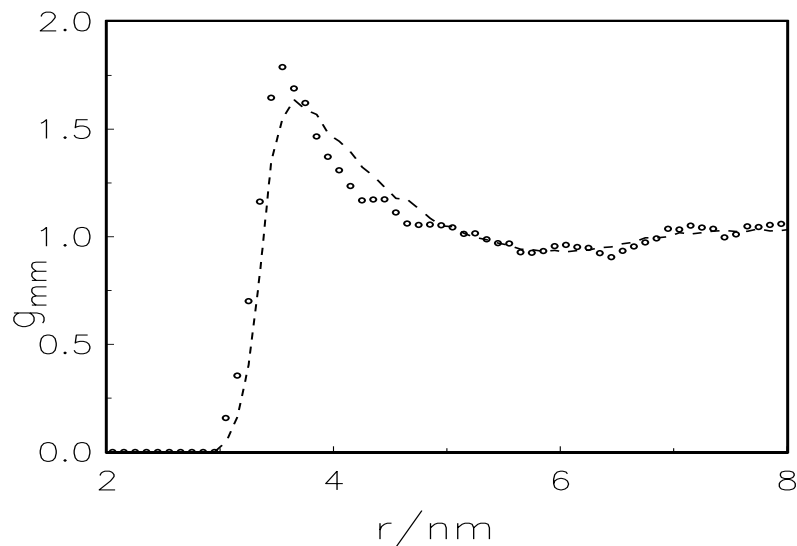
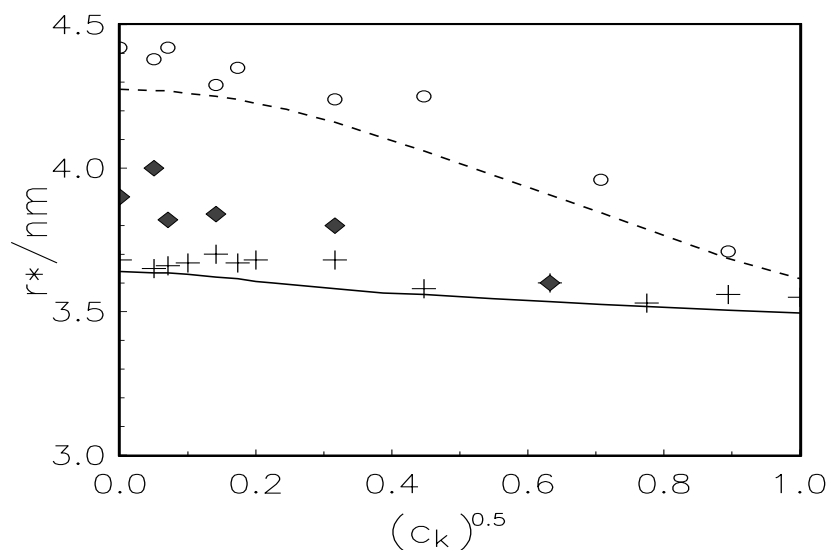Figure 2: The same as for Figure 1, but for solutions with divalent counterions.

Figure 3: Position of the first peak of the pair distribution function for macroions as a function of c_k. Monte Carlo results: solutions with monovalent counterions (open symbols), solutions with divalent counterions (crosses) all at $c_m = 0.02$ M. Diamonds denote results for a -20:+2/-1:+2 mixture at $c_m = 0.01$ M. HNC calculations are presented by lines: dashed curve - monovalent counterions, full curve - divalent counterions, both curves for $c_m = 0.02$ M.
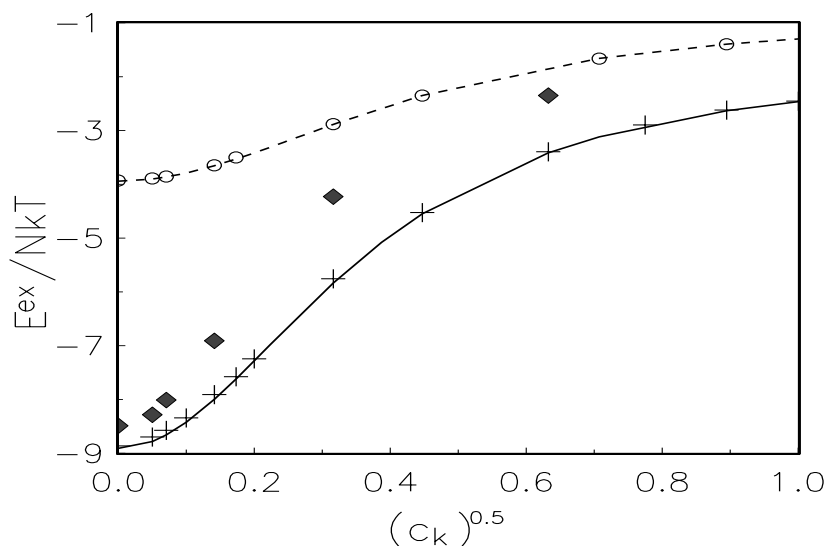
Figure 4: The excess energy per particle as a function of the square root of the co-ion concentration c_k. Monte Carlo results are denoted by symbols (open symbols - monovalent counterions, crosses - divalent counterions, both for $c_m = 0.02$ M) and the diamonds apply to a -20:+2/-1:+2 mixture at $c_m = 0.01$ M. The HNC data are shown by lines; monovalent counterions - dashed line, divalent counterions - full line, both at $c_m = 0.02$ M.

terions. The second conclusion is that strong correlations between the divalent counterions are not significantly affected by the presence of a simple electrolyte. For example, the position of the first peak in pdf for macroions moved from $r^* = 3.68$ ± 0.05 nm for salt-free solution at $c_m = 0.02$ M (cf also [9]) to 3.60 ± 0.05 nm, as observed in our Figure 2. The effect of addition of a low-molecular weight electrolyte on the distribution of macroions is more clearly seen in Figure 3. In this figure we plotted the position of the first peak r^* as a function of the concentration of co-ions, c_k. Open symbols denote Monte Carlo results for the mixture with monovalent counterions and crosses data obtained for mixtures with divalent counterions, both for $c_m = 0.02$ M. Filled symbols (diamonds) represent the Monte Carlo data for a -20:+2/-1:+2 mixture at lower concentration $c_m = 0.01$ M. For solutions with $z_c = +1$ we observe a decrease of r^* with increase in the co-ion concentration, while the solutions with divalent counterions seem to be less affected by the presence of a simple electrolyte. The HNC results for macroion concentration $c_m = 0.02$ M, presented by lines in this Figure, are in reasonable agreement with the computer data. In spite of considerable effort, no convergent HNC results were obtained for -20:+2/-1:+2 mixtures at $c_m = 0.01$ M.
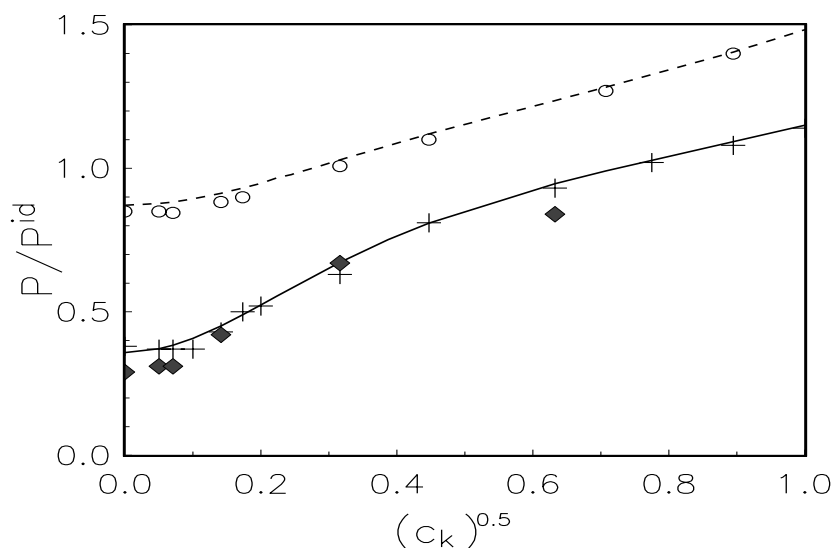
Figure 5: The osmotic coefficient as a function of the square root of c_k. Legend as for Figure 4.

In addition to their structure, thermodynamic parameters of mixtures of -20:z_c and -1:z_c electrolytes (z_c is either +1 or +2), were also studied. The excess internal energy per particle was calculated by [17]

$$\frac{E^{ex}}{N} = \frac{2\pi}{\rho_t} \sum_{i,j} \rho_i \rho_j \int_0^\infty u_{ij}(r) \ g_{ij}(r) \ r^2 \ dr, \tag{4}$$

where ρ_i is the number density of ionic species i and ρ_t is the total number density. The osmotic coefficient, defined as the ratio of the calculated pressure and ideal pressure $\phi = P/P^{id}$, was obtained via the virial route [17]:

$$\phi = 1 - \frac{2}{3} \frac{\pi\beta}{\rho_t} \sum_{i,j} \rho_i \rho_j \int_0^\infty u'_{ij}(r) \ g_{ij}(r) \ r^3 \ dr, \tag{5}$$

where the prime in Equation (5) denotes the derivative with respect to the coordinate r. These results are shown in Figures 4 and 5. As expected, the excess internal energy (Figure 4) and osmotic coefficient (Figure 5) increase with rising concentration of added low-molecular electrolyte. The agreement with the HNC calculation, the latter results being presented in Figure 5 by lines, is good.

Conclusions

The properties of highly asymmetric electrolytes are of interest for several problems in chemistry and biology [6, 7, 22]. In the present paper the Monte Carlo method

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and the integral equation theory in the HNC approximation were applied to model solutions containing macroions, co-ions and mono- or divalent counterions. More precisely, the effect of addition of a low-molecular weight electrolyte to solutions of macroions and counterions of different valencies was investigated. The calculations were performed for two different macroion concentrations, i.e. for $c_m = 0.01$ M and 0.02 M. The conclusion is that for solutions with divalent counterions even an excess of added simple electrolyte does not affect the macroion-macroion distribution appreciably. In parallel to the Monte Carlo simulations the HNC approximation was applied to the same model solution. The HNC theory, for the region of parameters where it was possible to obtain convergent results, is in good agreement with the simulation results for both structural and thermodynamic properties.

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Povzetek

V članku so predstavljeni novi rezultati za preprosti model raztopine micelov, dobljeni z Monte Carlo simulacijo in integralsko enačbo. Ioni so ponazorjeni kot toge kroglice z naboji v središčih. Razmerje premerov makroionov in protiionov je 3,0 nm : 0,4 nm, medtem ko je razmerje v naboju $-20 : z_c$, kjer je z_c lahko +1 ali +2. V prejšnjem članku (B. Hribar and V. Vlachy, *J. Phys. Chem. B*, **1997**, *101*, 3457-3459) smo ugotovili, da je razporeditev makroionov v raztopini močno odvisna od naboja protiionov. V raztopinah z enovalentnimi protiioni (-20:+1) so makroioni razporejeni na velikih razdaljah, medtem ko sta v raztopini z dvovalentnimi protiioni (-20:+2) dva makroiona najbolj verjetno razmaknjena le za plast protiionov. V pričujočem delu smo raziskali vpliv dodatka enostavnega elektrolita na razporeditev makroionov. Po pričakovanju se vrh porazdelitvene funkcije za makroione ob dodatku elektrolita pomakne k manjšim razdaljam. Ugotovili smo tudi, da dodatek elektrolita ne spremeni bistveno porazdelitve makroionov, če so v raztopinah prisotni dvovalentni protiioni. Poleg porazdelitvenih funkcij podajamo tudi rezultate za presežno notranjo energijo in osmozni tlak v odvisnosti od koncentracije dodanega elektrolita.