

Evidence of Electrostatic Attraction between Equally Charged Macroions Induced by Divalent Counterions

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Monte Carlo results are reported for solutions of macroions and counterions with asymmetries in charge of 20:1 and of 20:2 and asymmetry in size of 15:2. The ions are represented as charged hard spheres moving in a continuous dielectric. The results for divalent model electrolyte differ qualitatively from those for monovalent counterions. The macroion-counterion pair distribution function (pdf) indicates a very high accumulation of divalent ions about a macroion. This in turn yields an attraction between the like charged macroions; the location of the first peak in the macroion-macroion pdf suggests that there are one or two layers of counterions between the two macroions.

The equilibrium statistical thermodynamics of electrolytes in homogeneous and heterogeneous media is a topic of considerable practical and scientific importance. Colloidal solutions, charged interfaces, and polyelectrolytes are a few examples of such systems. In all these systems there is a strong Coulombic interaction between the fixed charge on the macroions (or on a surface) and mobile ions in solution. This interaction yields a nonuniform distribution of the small ions on the side of the solution, which is popularly called the electrical "double layer". Among the theoretical tools needed to describe these systems, the Poisson-Boltzmann equation plays an important role. It is an essential part of the classical DLVO theory¹ which is often used to explain the stability of colloidal solutions. According to the DLVO formalism, an overlap of the electrical double layer always yields a repulsive interaction. In other words, no attractive force can ever be observed between two surfaces having like charge embedded in an electrolyte solution.

Theoretical and experimental research carried out in the last 10 years seems to suggest that we need to revise this picture. Recently, two important papers on this subject have been published.^{2,3} These papers contain many references, so we will only mention the most important ones. The existence of an attractive force between like-charged macroions due to the counterion correlations was first predicted by Oosawa.⁴ The next contribution in this direction was a paper of Patey,⁵ but unfortunately, the hypernetted-chain approximation used in his study has a tendency to overestimate the attractive contribution. Computer simulations^{6–8} and anisotropic hypernetted-chain calculations^{3,9} for a primitive model electrolyte enclosed between two charged surfaces both confirmed the existence of an attractive interaction for divalent counterions present in the solution. In two related papers, Lozada-Cassou and co-workers^{10,11} investigated the influence of various boundary conditions on the force between two charged surfaces. In this context we also need to mention the work of Ray and Manning¹² and the recent calculation of Spalla and Belloni.¹³

On the experimental side we should mention a report of the attractive force between two mica surfaces.¹⁴ Also, in a number of papers Ise and co-workers (for a review, see ref 15) report unexplained void structures observed in highly charged colloidal systems. A "liquid-vapor" transition in colloidal dispersions was observed in experiments performed by Tata and co-workers.¹⁶ The bundle formation of rodlike polyelectrolytes,

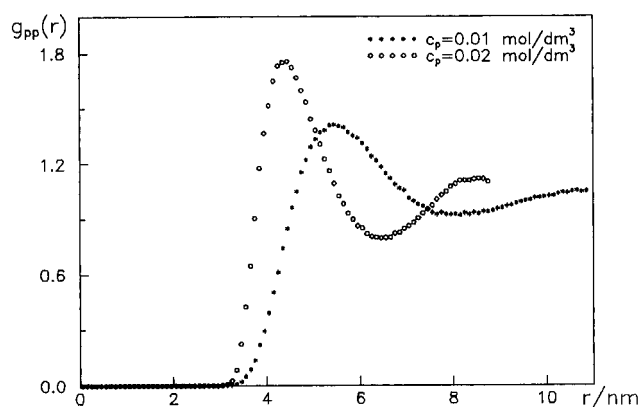


Figure 1. Macroion-macroion distribution functions obtained from Monte Carlo simulations for a $-20/+1$ electrolyte at $c = 0.01$ mol/dm³ (*, lower curve) and $c = 0.02$ mol/dm³ (○, upper curve).

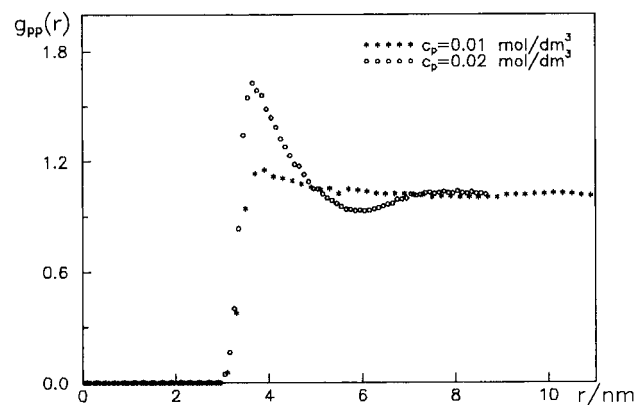


Figure 2. As for Figure 1, but for a $-20/+2$ electrolyte.

described by Tang et al.,¹⁷ is perhaps another example of attractive interactions triggered (or maybe caused) by multivalent counterions in the solution.

In this paper we present clear evidence of the electrostatic attraction between like charged macroions in a solution of divalent counterions, as obtained from computer simulations of the model solution. Our Monte Carlo study is based on the primitive model electrolyte; the ions are presented as charged hard spheres of different diameters. Asymmetric electrolytes with asymmetry in size of 15:2 and in charge of 20:1 and 20:2 were studied. The model supposes that the diameter of the micellar ions (macroions) is 3.0 nm and that of the counterions

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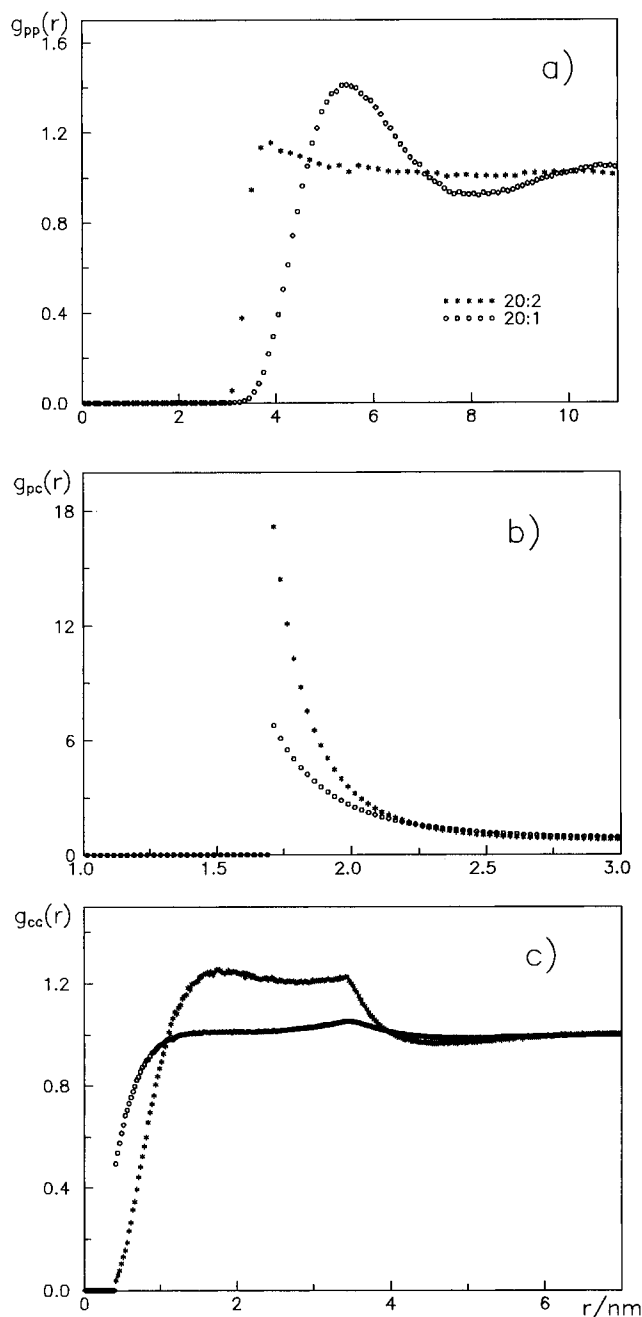


Figure 3. Monte Carlo results for $c = 0.01$ mol/dm³: (a) Macroion-macroion distribution function for 20:1 electrolyte (○, upper curve) and 20:2 electrolyte (*, lower curve); (b) macroion-counterion distribution function for 20:1 electrolyte (○, lower curve) and 20:2 electrolyte (*, upper curve); (c) counterion-counterion distribution function for 20:1 electrolyte (○, lower curve) and 20:2 electrolyte (*, upper curve).

0.4 nm. No simple electrolyte is present, and the solution is treated as a continuous dielectric with dielectric constant ϵ . All calculations presented apply to $T = 298$ K, where the Bjerrum length $e_0^2/(4\pi\epsilon k_B T)$ is 0.715 nm. These values of parameters were chosen to facilitate comparison with previous calculations of model micellar solutions.^{18–20} The canonical Monte Carlo method applied here uses the Ewald summation to account for finite size effects. The calculations were performed in a cubic box, for a system of 64 macroions and an equivalent number of counterions. For solutions with divalent counterions, we performed a limited number of calculations on a system with 128 macroions. Since no difference between the two calculations was found, we report only the data for 64 macroions. The statistics were collected over 70 million attempted configura-

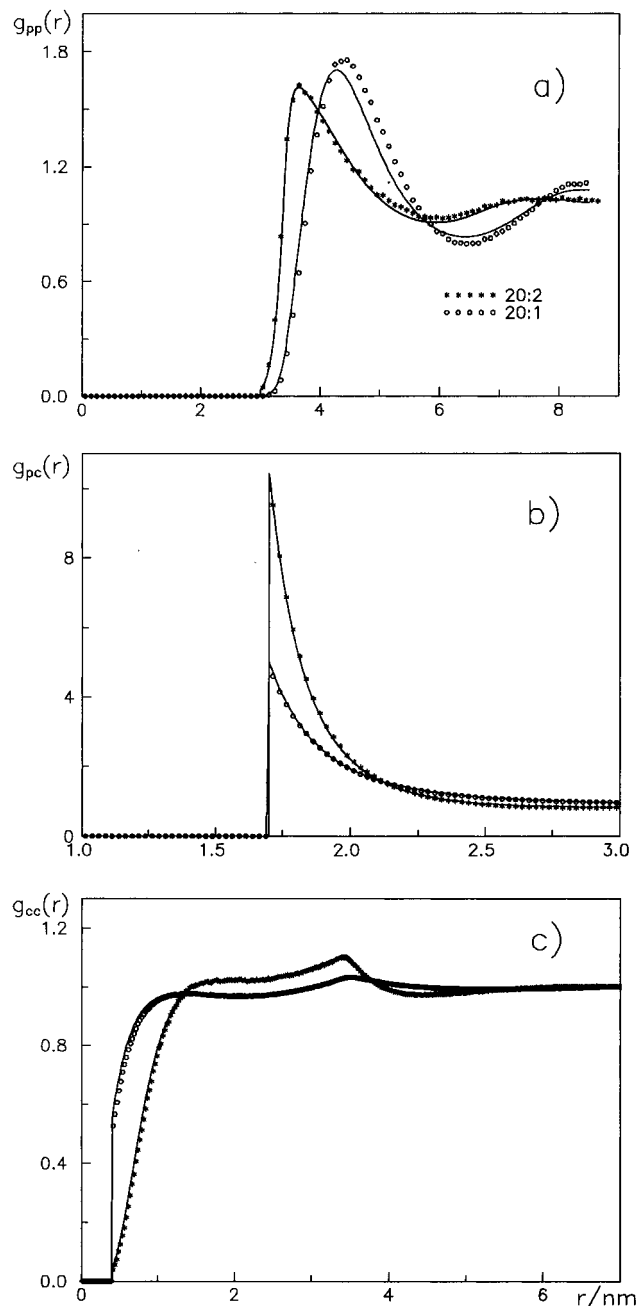


Figure 4. Monte Carlo and HNC results (lines) for $c = 0.02$ mol/dm³. Notations as for Figure 3.

tions, after an equilibration run of 5 million configurations. Some details of the method were described in our previous papers.^{18–20}

We begin the discussion by considering the pair distribution function (pdf) for monovalent counterions, i.e. for a 20:1 electrolyte, first. Figure 1 shows the macroion-macroion distribution function at two different concentrations, $c = 0.01$ M and $c = 0.02$ M, respectively. As expected, the first peak of the pair distribution function is shifted toward larger distances if the concentration of macroions in solution decreases. This is clearly a consequence of the repulsive interaction between the equally charged macroions, and it has been observed in several previous studies.^{18–20}

We consider next the results for 20:2 model electrolytes. Again the pair correlation function was studied for two concentrations of macroions: $c = 0.01$ M and $c = 0.02$ M.

The results for divalent counterions shown in Figure 2 are remarkably different from those for the 20:1 model electrolyte. In contrast to the results for monovalent counterions, the first

peak of the pair distribution function for a 20:2 electrolyte (Figure 2) does *not* change its position upon dilution. For both concentrations studied here it is located at about 3.8 nm. This means that there is on the average one layer or two of divalent counterions between two macroions. The effect of divalent counterions on the correlation between macroions is shown even more clearly in Figures 3a and 4a. Here, for better comparison, the pdf data for monovalent and for divalent counterions at a particular concentration (the same results as previously plotted in Figures 1 and 2) are shown in the same figure. Clearly, the structure of both solutions is substantially different. By replacement of the monovalent counterions with divalent ones, the peak of the distribution function corresponding to the first layer of neighbors is shifted toward smaller distances. Also, the solution with divalent counterions is less structured, there is very little structure seen beyond the first peak for these concentrations. The results presented by full lines (Figure 4) were obtained by the hypernetted-chain (HNC) integral equation theory (see, for example, ref 20). In spite of considerable effort, no convergent result of the HNC integral equation could be obtained for the less concentrated (0.01 M) solution.

The results presented above are a consequence of the strong correlation between the divalent counterions in the double layer around the spherical macroions. In order to illustrate this effect, other pair distribution functions were also calculated. Figures 3b and 4b present the concentration profiles for mono- and divalent counterions around the macroion for $c = 0.01$ M and $c = 0.02$ M solutions, respectively. The graphs reveal a much higher accumulation of the divalent counterions around a macroion compared to the solution with monovalent counterions at the same concentration. For divalent counterions the electrical double layer is thinner and has a nonmonotonic character with a broad minimum. The equivalent counterion-counterion distributions are shown in Figures 3c and 4c. Again it is easy to see that the correlations between divalent ions are stronger than for monovalent counterions, and, as expected, the deviations of the pdf from unity are larger at lower concentrations of macroions. Note that the shape of the counterion-counterion distribution function changes on increasing the concentration. In the second case, i.e. for more concentrated solution, the highest probability of finding the second counterion is just on the opposite side of the macroion.

The attraction between macroions in solution can also be obtained through the so-called "depletion" mechanism.²¹ As shown in several papers,^{22–24} the addition of a neutral or charged component to the solution may yield an attraction between the macroions if the volume fraction of added component is high.

However, the structure of the solution, as seen by the macroion-macroion pdf, is different in this case; the two macroions are in close contact when the depletion interaction is the strongest. This is not the case in the example presented in this work, where the attraction comes from sharing the layer of counterions.

The study presented in this Letter proves that attraction between like charged macroions is possible if multivalent counterions are present in the solution. In future, in more complete work, we intend to study the system with a mixture of mono- and divalent counterions to investigate how the repulsion is turned into attraction by a gradual replacement of the monovalent counterions by divalent ones.

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