The influence of concentration and ionic strength on the cluster structure of highly charged electrolyte solutions

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The structure of 2 : 2 electrolyte solutions at several concentrations—obtained through stochastic dynamics simulations—is investigated by means of a cluster analysis. It is shown that most of the ions in the systems at the higher concentrations studied (up to 2 M) are linked at short distances, forming large clusters, even though the mean number of neighbours is only about two. As the concentration decreases there is a distinct short and long-range behaviour. The clustering observed at short distances is similar to that obtained in the more concentrated solutions. This means that within this region the charges of the nearby ions are individually perceived. Conversely, at long distances, the effect of the surrounding charges becomes more diffuse; the properties seem to be rather dependent on the mean field and are similar to those of a 1 : 1 electrolyte at the same ionic strength. Although no neutral pairs seem to be present in the more dilute solution investigated in this paper (0·25 M), the concentration dependence of our results suggests that the Bjerrum picture (and recent theories of the ionic association) should accurately describe the clustering at lower concentrations.

1. Introduction

The study of the association between the ions in electrolyte solutions was initiated by Bjerrum [1] only three years after the classic Debye–Hückel theory appeared. Using the same approach as the Bjerrum theory, Fuoss and Kraus [2] devised a theory to explain the minimum in conductivity due to triple ion formation. But the investigation of the ionic association (beyond the strict ion-pairing) suffered a certain impasse. The situation did not change very much despite the general success of integral equation theories (especially the hypernetted chain (HNC) equation), partly because of the intrinsic lack of information on the ion–ion pair correlation functions but also due to the difficulties of the theory when dealing with strong interionic interactions (several times greater than the thermal energy) [3–5]. Nevertheless, such studies yielded reasonable suggestions of the appearance of complex aggregates in highly charge electrolytes [6]. In recent years there has been a growing interest in this problem. The presence of triplets and even higher aggregates is now well established both theoretically [7, 8] and by computer simulation [9, 10]

In our previous paper [9], the structure of two model aqueous solutions—1 : 1 and 2 : 2 electrolytes both at 1 M concentration—simulated by Langevin dynamics

was analysed within a cluster approach. The study revealed some new features not easily noticeable in a two-particle correlations basis. By using several ion–ion distances as a connectivity criterion it was shown that the particles can be arranged at distances beyond that corresponding to the first maximum in the unlike-pairs correlation function. The average ion of the 2 : 2 electrolyte has very few neighbours (about two) with opposite sign charges within the first coordination shell while the number of ions carrying the same charge within the same volume is less than unity. The spanning of this local structure to longer ranges brings on the existence of large clusters formed by arrangements of ions with alternating positive and negative charges in a (topological) chain-like ordering; such clusters concern a relevant proportion of the total number of ions. On the contrary, the classical 'charge cloud' picture seemed to give a fair description of the structural trends of the 1 : 1 aqueous solution.

Since the systems studied were at the same concentration, an unambiguous comparison of the structures in terms of absolute distances was possible. But, at the same time, it was not clear whether such contrasted features were due to the differences in their ionic strength or, strictly speaking, to the disparity of the ionic charge. Our feeling was that the structure observed in the highly charged solution must be the result of strong interactions with the very nearest particles rather than the effect of a mean electrical field produced by the ensemble of ions, but this could not be demonstrated unless other systems were investigated. Besides, it is not clear how the results presented in I are compatible with the Bjerrum and more recent theories of ionic association [1, 7]. This work attempts to clarify these points; it is thus devoted to the study of the influence of concentration and ionic strength on the clustering in electrolyte solutions modelled by Langevin dynamics.

The article is organized as follows. Section 2 describes the interaction model and the state points investigated in this work. A brief description of the technical details of the simulations is also included. As the analysis of the ion–ion pair correlation and derived functions anticipate in some way more complex structural issues [6, 9], we dedicate section 3 to the discussion of the two-particle correlations results. Special emphasis is put on the behaviour of the excess charge and the appearance by Stillinger and Lovett as a consequence of the second-moment condition [11]. In section 4 we focus our attention on the cluster analysis. A discussion of the structural features observed in simple electrolytes and its outcome on more complex systems concludes this report.

2. Model electrolytes and simulation details

The particular form of stochastic dynamics and potential model used in this work have been described elsewhere [12, 13], so only a sketch will be given for completeness. The generalized Langevin equation (GLE) for the motion of a particle is

$$\dot{p}(t) = -\int_0^t f(t - s)p(s)\,\mathrm{d}s + R(t) + X(t), \tag{1}$$

where $p(t)$ is one of the cartesian components of momentum of the Brownian particle, R, that of the random force and X that of the external force, and $f(t)$

represents the memory function. There are several supplementary conditions,

$$\left.\begin{array}{l}\langle R(t)p(0)\rangle = 0, \quad \text{if } t > 0, \\ \langle R(t)\rangle = 0,\end{array}\right\} \tag{2}$$

and

$$\langle p^2\rangle = mkT.$$

The mass of the Brownian particle is m and $\langle\ldots\rangle$ denotes an average over the equilibrium ensemble. In addition, the random forces obey the second fluctuation–dissipation theorem [14]

$$\langle R(t)R(0)\rangle = \langle p^2\rangle f(t). \tag{3}$$

If the random force R is chosen to be constant for time steps of duration t_s such that $t_s < t_p$ then the GLE transforms into the strict Langevin equation [12]

$$\dot{p}(t) = -p(t)/t_p + R(t) + X(t), \tag{4}$$

with the correlation time for the momentum t_p given by

$$t_p t_s = 2\langle p^2\rangle/\langle R^2\rangle, \tag{5}$$

and thus

$$\langle R^2\rangle = 2(kT)^2/D^0 t_s, \tag{6}$$

where D^0 stands for the diffusion coefficient in the absence of external forces.

The pair potential is given by the expression [15]

$$u_{jj'}(r) = B\left[(\sigma_j + \sigma_{j'})/r\right]^{n_c} - e_j e_{j'}/\epsilon r, \tag{7}$$

where e_j is the charge and σ_j the Pauling radius of the ion j. The parameter n_c modifies the slope of the repulsive forces and ϵ, the relative dielectric constant of the solvent, the strength of the Coulombic interactions. The coefficient is

$$B = A|z_j z_{j'}|e^2/n_c(\sigma_j + \sigma_{j'}), \tag{8}$$

where A is the Madelung constant, z_j the electrovalence of j and e is the electronic charge. In order to enhance the effect of the Coulombic forces, we have fixed the dielectric constant at $19\cdot8$ and the ionic valences at 1. It is to be expected that the clustering in this system would be barely distinguishable from that with $z_+ = z_- = 2$ and $\epsilon = 78\cdot5$; for simplicity we will refer to it as a 2 : 2 aqueous solution. In fact, more important are the values for the repulsive exponent and the ionic radii because they determine the position of the first peak in the unlike charge pair distribution functions. The choice $n_c = 9$ $\sigma_+ = \sigma_- = 1\cdot38\,\text{Å}$ produces a peak at the same position as a restrictive primitive model with a $4\cdot2\,\text{Å}$ diameter [4]. Although the minimum image method might suffice [16], the Ewald method has been used to account for the interactions with the ions outside the cell. The self diffusion coefficients of cations and anions at infinite dilution, D^0, are $2\cdot03 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$, the masses 360 (see [13] for a discussion concerning this point) and the timestep $0\cdot5 \times 10^{-13}\,\text{s}$.

The runs have been carried out at $298\cdot16\,\text{K}$ and the volume of the cell was chosen so that the ion number density was the same as for $0\cdot25$, $0\cdot50$, 1 and 2 M solutions respectively formed by a 216 ionic particles sample. As the results for a 1 : 1 electrolyte at 1 M concentration has been previously reported [9] it is possible to study the

Table 1. System parameters and osmotic coefficients for the 2 : 2 electrolyte solutions. M is the molar concentration, κ the inverse Debye length and $a = 4\cdot2\,\text{Å}$ the hard-sphere diameter of an equivalent restrictive primitive model (see the text). The third and fourth columns are the number of steps of each run and the results for the osmotic coefficient ϕ

M	κa	N	ϕ
0·25	1·95	16000	0·59
0·5	1·38	10000	0·44
1	0·98	10000	0·45
2	0·69	12000	0·84

influence of both the concentration and the ionic strength on the clustering.The configurations generated and the quantities of interest were stored in disk at intervals of four steps for later analysis. The end of the equilibration process was determined by the asymptotic behaviour of the potential energies and the osmotic pressures in successive subaverages over 100 configurations. The number of steps for the production phase are given in table 1, the total simulation time lasting between 500 and 800 ps. Also shown in table 1 are the results for the osmotic coefficients. Although we do not attempt to model any particular real electrolyte, the osmotic coefficients are in reasonable agreement with the experimental values for several divalent sulphate solutions [17]. Some dynamical results were reported in [18].

Table 2. Numerical values of the ion–ion distribution functions, coordination numbers and excess charge at characteristic distances. Variation with concentration for 2 : 2 electrolytes

M	r^*	g_{+-}	g_{++}	n_{+-}	n_{++}	$1 - q_{\text{exc}}$
First maximum g_{+-}						
0·25	0·27	9·0	0·03	0·13	0	0·87
0·5	0·37	4·9	0·07	0·18	0·002	0·83
1	0·47	3·3	0·10	0·28	0·005	0·72
2	0·56	2·7	0·11	0·34	0·008	0·67
First maximum g_{++} $\approx$ first min. g_{+-}						
0·25	0·72	1·11	1·08	1·5	0·6	0.09
0·5	0·76	1·07	1·08	1·7	0·6	−0·06
1	1·00	0·92	1·09	2·8	1·6	−0·20
2	1·13	0·89	1·11	3·6	2·3	−0·27
First electroneutral sphere						
0·25	—	—	—	—	—	—
0·5	0·64	1·3	0·87	1·2	0·24	0
1	0·65	1·6	0·58	1·1	0·14	0
2	0·68	1·8	0·44	1·1	0·11	0
First maximum q_{exc}						
0·25	—	—	—	—	—	—
0·5	0·76	1·07	1·08	1·7	0·60	−0·06
1	0·86	1·00	1·00	2·0	0·75	−0·28
2	0·93	0·98	0·98	2·3	0·86	−0·47

3. Pair correlations and derived functions

Table 2 shows the numerical values of the ion–ion distribution functions, g_{++} and g_{+-}, together with the running coordination numbers defined by

$$n_{ij} = \rho_j \int_0^r 4\pi r'^2 g_{ij}(r')\, dr', \tag{9}$$

where ρ_j is the bulk number density of species j. In the case of unlike charge functions, the mean values of the $++$ and $--$ contributions are used. Lengths are given in reduced units, i.e., expressed in terms of the distance between nearest neighbours in a *halite* lattice with the same number density.

$$r_{ij}^* = r_{ij}/(\rho_+ + \rho_-)^{-1/3}. \tag{10}$$

It has been noted [9] that the analysis of the structure of electrolyte solutions solely in terms of the g's may be misleading. For instance, it is well established that as the concentration decreases the value at the first peak of the unlike charge pair distribution function increases. But this is not evidence of a more structured system since the curve decays sharply to unity in dilute solutions. In contrast, at higher concentrations the maximum in g_{+-} has a lower value but the curve does not decay monotonically, having a minimum and even a second maximum suggestive of a layer ordering. Besides, the region of influence of a given ion can extend far beyond the first maximum of the unlike ion pair distribution function. The remark is more evident as the concentration decreases. Figure 1 displays the curves at $c = 0.25\,\mathrm{M}$ (incidentally, they are in accordance with previous simulations [4, 10, 16] for a $0.20\,\mathrm{M}$ aqueous solution). Despite the impressive sharp peak in g_{+-}, at these distances, the coordination numbers are such that only a small amount of the charge (about 13%) is compensated. The excess charge, defined through the expression

$$q_{\mathrm{exc}}(r) = n_{+-}(r) - n_{++}(r), \tag{11}$$

represents the charge cancelled by the ions within a distance r of a given particle expressed in units of the ions charge ze. Equivalently, $1 - q_{\mathrm{exc}}(r)$ gives information about the mean value of the *net charge*—in ze units—contained in a sphere of radius
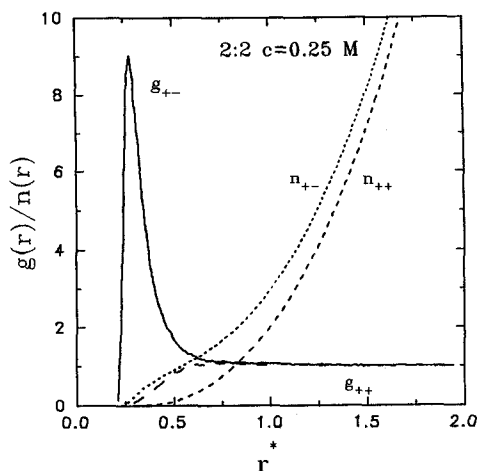

Figure 1. The like- and unlike-charge pair distribution functions together with the running coordination numbers for the 2 : 2 electrolyte at $0.25\,\mathrm{M}$ concentration.

r from the central particle. This function is important because the net charge must be intermediate between that of two well-known ideal systems. In the limit of infinite dilution, $1 - q_{exc}$ is a decaying function which approaches asymptotically to zero as $r \to \infty$. On the other hand, the *net charge* is an infinitely oscillating curve for a perfect ionic crystal. Stillinger and Lovett [11] demonstrated a second moment condition to be fulfilled by any arbitrary mixture of electrolytes of unrestricted charge species. One important consequence is the appearance of charge oscillations in the ion atmosphere at sufficiently high concentrations. For the restricted primitive model (RPM) model the critical concentration is at most that corresponding to $\kappa a = \sqrt{6}$. This is actually an overestimation of the limit and Stillinger and Lovett [11] themselves suggested the interval 1·0–1·5 as a more likely limit range. In table 1 we show the κa values of our solutions (we assume an equivalent RPM model with $a = 4·2$ Å).

The concentration dependences of $1 - q_{exc}$ for our 2 : 2 aqueous solutions are shown in figure 2 (see also table 2 for the numerical values at characteristic distances). As expected, the amplitude of the charge oscillations is greater in the more concentrated solutions. The value of $1 - q_{exc}$ at the first minimum indicates that the net charge within the first layer significantly exceeds the cancellation of that of the central ion (by almost 50%) in the 2 M system. It has a definite second layer and (at least) a third one with alternate charge signs. When the concentration decreases so does the amplitude of the oscillations. For the lower concentration studied the local oscillations are so damped that they cannot invert the sign of the net charge. Our results indicate that the critical concentration for the appearance of charge oscillations correspond to an effective value of κa slightly below unity. The curve for the 0·25 M solution deserves special comment. At short distances, it behaves like the concentrated solutions; the curves are parallel because the hard repulsive core obviously does not depend on (and thus it does not scale with) the number density. Conversely, the long tail observed in the net charge of the 2 : 2 0·25 M electrolyte is characteristic of dilute solutions.

Figure 3 shows the results for the net charge in systems differing only in ionic strength, ionic charge or concentration. The long-range behaviour of the
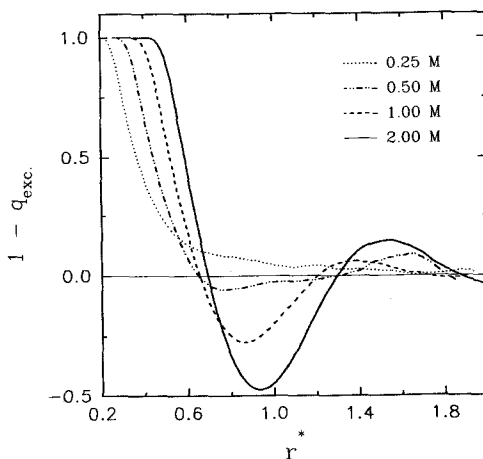

Figure 2. The net charge $1 - q_{exc}(r^*)$ as a function of distance at different concentrations (2 : 2 electrolytes).
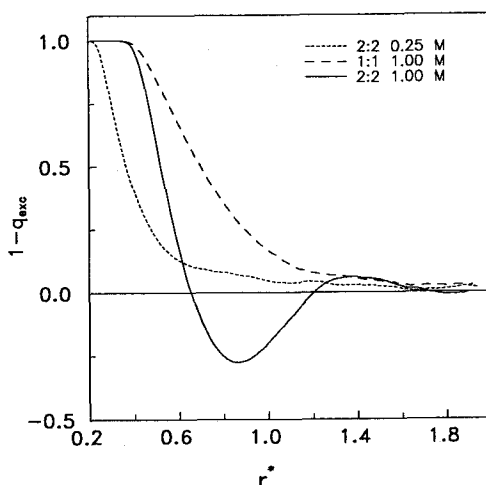
Figure 3. Comparison of the net charge $1 - q_{exc}(r^*)$ for systems with the same ionic strength ionic charge or concentration.

$2 : 2\ 0\cdot25$ M solution is similar to that of the $1 : 1$ 1 M solution which has the same ionic strength, the short range being quite different. Just the opposite holds for the comparison with systems with the same ionic charge and different concentration. Finally, systems at the same concentration have no common features. Figure 3 demonstrates that—at least in the interval of concentrations and ionic charges investigated in this work—the effect of the ionic charge is specially important at short distances while the long-range ordering is primarily determined by the ionic strength. This supports a modern day formulation of the Bjerrum association theory [7] which split the total pair potential energy into associative (at short distances) and non-associative (at long distances) parts.

The most striking feature of the excess charge results for our models of relatively concentrated solutions in a medium with a low dielectric constant is the number of ions involved in the first coordination and successive shells. Assuming that we can determine it through the extrema in the excess charge, the number of unlike particles within the first coordination shell is about 2 (table 2) and increases with concentration. Further progress in the description of the underlying structure of these aqueous solutions cannot be expected from the analysis of pair correlation functions. We continue our study with the cluster analysis which has proven [4, 9] to be a fruitful tool in the investigation of the structure of electrolyte solutions.

4. Cluster analysis

We have studied the clustering properties of every four configurations generated by the stochastic dynamics simulations. Two particles j, j' are considered to be in the same cluster if the distance between them is lower than a given value, R_{cl}. Also, it is a condition for two ions to be considered linked that they carry charges of unlike sign

$$\left.\begin{array}{c} r_{jj'} < R_{cl}, \\ \text{and} \\ z_j = -z_j'. \end{array}\right\} \tag{12}$$
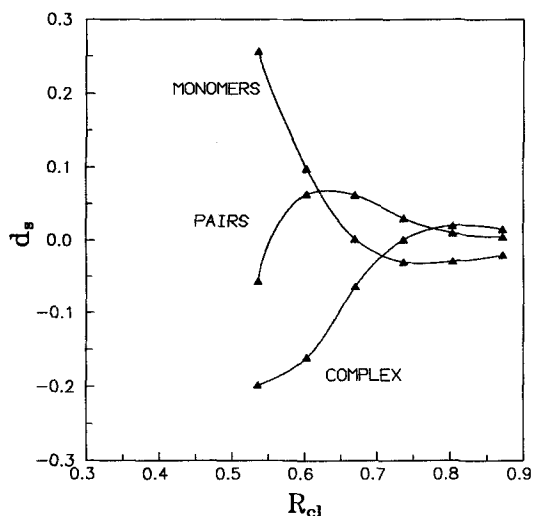
Figure 4. Excess number of ions in different types of clusters for the 2 : 2 electrolyte at 2 M concentration relative to those for the random system.

The condition guarantees some significance (and stability) to the clusters so obtained. A wide range of R_{cl} values has been used, from that at which the repulsive forces keep the majority of ions apart up to distances corresponding to the formation of a percolating cluster. We identified several types of clusters but for the presentation of results we will restrict ourselves to monomers (isolated ions), dimers and great aggregates globally referred to as complex clusters. In figures 4 and 5 we represent—for the 2 M and 0·25 M solutions respectively—the fraction of ions ascribed to a given type of cluster as a function of R_{cl}. In order to remove non-structural features we have subtracted the corresponding values for a system of non-interacting (i.e., randomly distributed) particles at the same number density.

In the system at 2 M concentration, the effect of the repulsive forces is reflected in the high number of isolated ions—relative to the random system—for the smaller
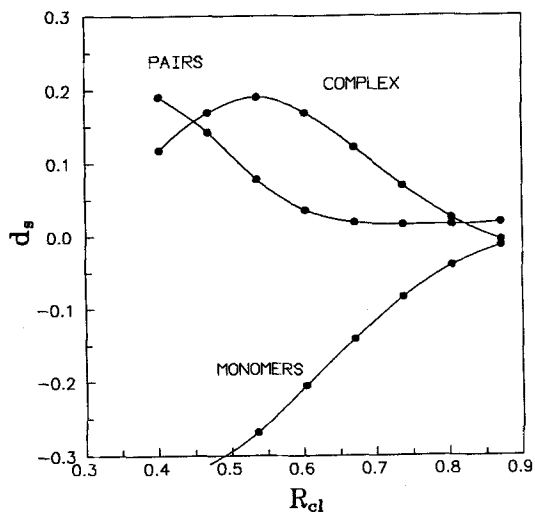

Figure 5. As figure 4, but at 0·25 M concentration.

clustering distances R_{cl} studied (note that they are close to the position of the peak in g_{+-}). The excess number of complex clusters is negative while the few numbers of clusters found are pairs. There is a very small interval of R_{cl} values for which the monomers aggregate in pairs while the excess number of complex clusters remains almost constant. Beyond that point both the number of monomers and pairs decrease with larger R_{cl} while ions in higher clusters sharply increase. This means that true pairs are rather scarce in the 2 M solution, taken in a more general sense to include large clusters. At this concentration, a strong organization of the ions occurs at distances—say it is denoted by the inflection point of the complex clusters curve— close to that of the electroneutral sphere; there the running coordination number n_{+-} is only about 1·1. The excess number of ions in large clusters reaches a maximum which includes about 80% of the total particles and is achieved at $R_{cl} \approx 0\cdot8$ well before the maximum of the excess charge. One could be tempted to stress the resemblances to a molten salt structure but we must recall that the number of unlike charged nearest neighbours is much smaller in the aqueous electrolyte (see table 2) than in a molten salt.

As the range of the repulsive forces is considerably shorter than the mean distances between ions in the 0·25 M solution, its effect on the clustering is not noticeable at the R_{cl} investigated. This is an expected departure, having regard to the above results. More significant are the differences in the monomer curves. Conversely to the 2 M system, the excess number of isolated ions is now negative for all of the clustering distances; the smaller R_{cl}, the higher excess number of monomers. The excess number of pairs is highly positive at short distances. In fact, it corresponds approximately to the region where the charge of a given ion is mostly cancelled (see table 2). This curve has a rather slow decay somewhat, supporting the actual existence of almost neutral pairs in accordance with the Bjerrum picture. When the clustering distance is taken to be about 0·6, the system appears as organized in a more complex manner (the number of ions in trimers and larger aggregates reaches a maximum). The value at the peak of the complex clusters curve is considerably higher than that for the 2 M solution but the slope is here much less
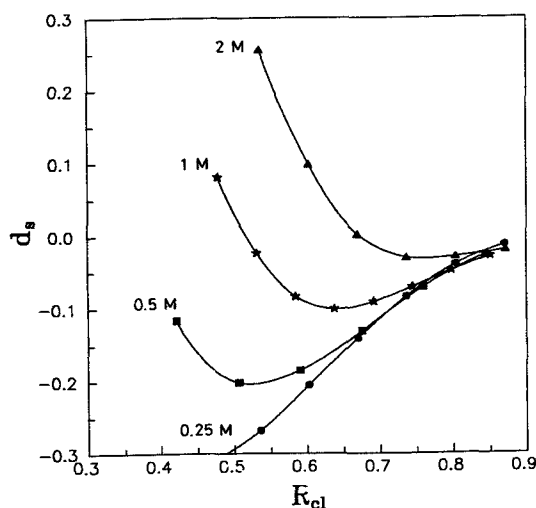

Figure 6. Excess number of isolated ions (monomers) as a function of the clustering distance R_{cl} at different concentrations (2 : 2 electrolytes).
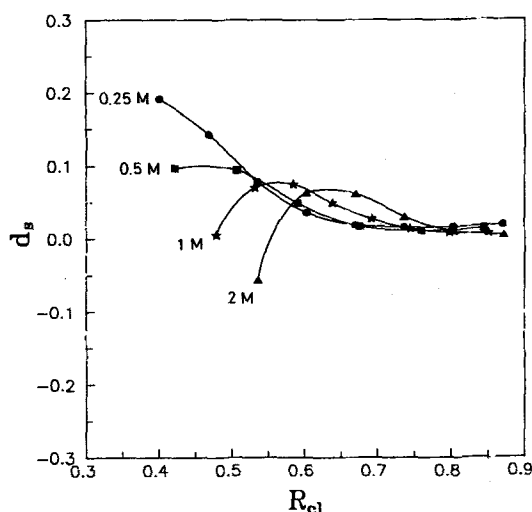
Figure 7. As figure 6, but for ions in pairs.

pronounced, indicating that the aggregation of ions in clusters is not as critical as in the more concentrated electrolyte. The total number of ions in complex clusters at the peak is now about 55. But, as the $1 - q_{exc}$ plot shows, the region of influence of the ions extends beyond that point. This suggests a continuous transition from the immediate surroundings where each ion perceives distinctly the interaction with the few nearby particles to distances far away whose effects appear through the mean field produced by the charge distribution.

Figures 6–8 show the concentration dependence of the results for each type of cluster. For high R_{cl} they scale with $\rho^{-1/3}$ so all the curves in each plot converge to the non-interacting system (i.e., the excess number of ions approaches zero) at about the same value. As mentioned above, the short-range behaviour depends rather on the absolute distances than on the reduced ones. Accordingly, the positions of the
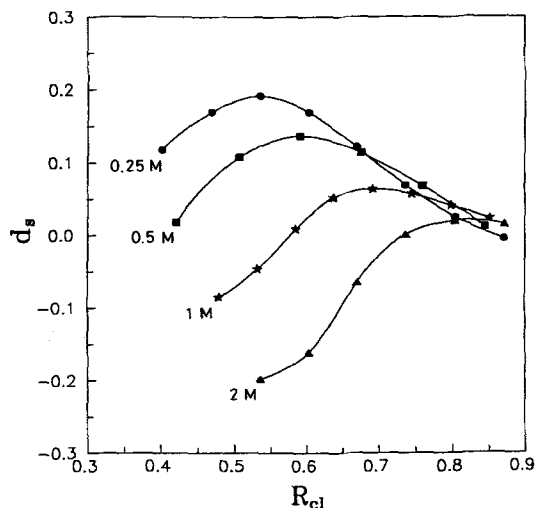

Figure 8. As figure 6, but for ions in complex aggregates (containing three or more ions).

extrema are shifted towards smaller reduced distances as the concentration increases. It is to be noted that the less concentrated solutions have more pronounced departures from the non-interacting system. The heights of the peaks of the dimer curves indicate that the actual existence of neutral parts is restricted to (relatively) dilute solutions. It can be misleading that the 2 M solution has a negative excess number of ions in complex aggregates for most of the clustering distances. Such a result only indicates that the repulsive forces keep the ions apart up to distances close to the mean separation. When the distance of analysis lies beyond the range of the repulsive interactions the departures become positive. Unfortunately, no direct comparison can be made with previous clustering studies. Smith *et al.* [10] have investigated a 2 : 2 0·2 M electrolyte with $R_{cl} = 8·4$ Å and founded the fraction of complex clusters to be 0·38. Our value for a 2 : 2 0·25 aqueous solution with $R_{cl} = 9$ Å is 0·45 which is consistent with the previous one since the increase in both concentration and clustering distance enhance the ionic association.

The preceding discussion put the emphasis in the departures from the non-interacting system so no information is provided about the actual cluster size and the number of particles involved. This is partially answered in figure 9 where the mean cluster size, $\langle S \rangle$, is depicted for 2 : 2 electrolytes at various concentrations. $\langle S \rangle$ is defined in terms of the number of ions N_s in clusters of size s as

$$\begin{aligned} \langle S \rangle &= \sum w_s s \\ &= \sum s^2 N_s / \sum s N_s. \end{aligned} \tag{13}$$

There are other possible definitions of the mean cluster size but we have chosen this one because the summation is weighted with the probability of occurrence of each cluster size, w_s. Thus, $\langle S \rangle$ describes how large on average is the cluster we are hitting when we point randomly to an ion [19]. For low R_{cl} the mean cluster size curve is flat but for $R_{cl} \approx 0·8$ it rises exponentially. The slope increases with concentration and thus the different curves cross when $\langle S \rangle$ is still very small (figure 9). This is a
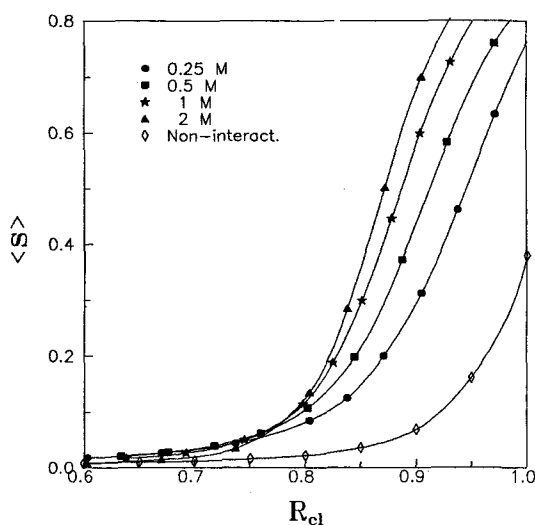

Figure 9. Mean cluster size as a function of the clustering distance at different concentrations (2 : 2 electrolytes).
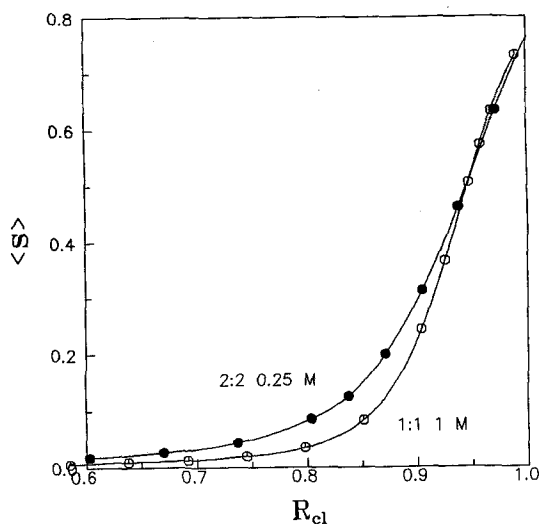
Figure 10. As figure 9, but for systems with the same ionic strength.

confirmation of the transition between the Bjerrum regime at low concentrations and the complex cluster properties of concentrated solutions. Note that these functions have been obtained in a finite size system, so the appearance of very large clusters is not possible. As a consequence, the curves have an inflection point. Beyond this point the departures with regard to an infinite system become important, so the slopes of the curves decrease instead of being exponentially increasing. Taking this effect into account it seems that the more concentrated solutions would have a mean cluster size close to unity at distances quite below than that of the nearest neighbours separation in a lattice. It is to be concluded that the are actually made of only one big cluster involving most of the ions. To stress the importance of this conclusion, let us recall that the clustering criterion restricts the links to unlike charged particles. Figure 10 displays the mean cluster size for two solutions with the same ionic strength. The 1 : 1 electrolyte curve rises only when R_{cl} is beyond 0·9, which is about the nearest neighbour distance in a slightly distorted lattice; the large clusters so obtained are rather irrelevant. Again, the results for a system with the same ionic strength (2 : 2 0·25 M) are coincident at large distances while the short range behaviour is distinct.

5. Concluding remarks

In this paper it is shown that the main structural feature of the 2 : 2 electrolytes at relatively high concentrations is the complexity of the clustering. The ions are organized in clusters linking unlike charged ions. In addition, a significant proportion of the ions are involved in the cluster despite the fact that the number of neighbours in the first coordination shell is about two.

It has also been demonstrated that this is not due to long-range effects but the organization is brought about by the strong electrostatic interactions in the short-medium distance range. This is in agreement with previous works showing that effective short-ranged potentials account for the properties of highly charged ionic systems [20]. When the concentration diminishes the mean distance between particles

is too large for the electrostatic forces to organize the whole system and there appear two regions. Any ion in the immediate vicinity of a given one is directly influenced, so at short distances the electrostatic interactions between are discrete. But at large distances the effects are averaged and the mean field forces characteristic of dilute electrolytes are manifest. Even if no true pairs seem to be present in any of the solutions studied, the dependence on concentration of this different short and long-range behaviour suggests that neutral pairs would appear in dilute 2 : 2 electrolytes.

There remain some questions concerning the validity of the results in real electrolytes. The ion–ion interaction model employed in this work has been widely used in the past with great success. Recently, new ionic potentials (obtained by averaging the effect of the solvent particles) have been obtained from integral equation calculations [21]. The oscillatory shape of these so-called mean field potentials (MFPs) is consistent with the ion–ion pair correlation functions determined from neutron diffraction experiments [22] and has been confirmed by computer simulation studies [23, 24]. Nevertheless, the disparity of the MFPs reported by different authors does not allow one to assess the importance of the effect of the oscillations on the cluster properties. Besides, to our knowledge, no such models have been proposed for 2 : 2 electrolytes. Exploratory simulations using functions with oscillations of similar amplitude to that of 1 : 1 electrolytes indicate that the clustering is enhanced [25].

When the electrolyte is in the vicinity of rigid charged systems (charged walls, polyelectrolytes) it is to be expected that the inherent electrolyte structure can be coupled with that of the rigid body which would result in a noticeable increase of the lifetime and stability of the ionic clustering. This could provide a way to explain the role of the ions in the salt dependent stability of certain complex systems. For example, concepts such as 'bridge' or 'discrete-ions' have been suggested in the past to explain the stability of colloids [26]. The same kind of phenomena could help in the understanding of salt induced conformational transitions of biopolymers (such as the *B* to *Z*-DNA [27–30]).

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