

# Ionic association in electrolyte solutions: A Voronoi polyhedra analysis

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Voronoi polyhedra (VP) analysis of ionic solutions generated via Monte Carlo simulations for a wide range of concentrations and ionic charges are reported. The properties investigated are the VP volumes, VP surface shared with unlike/like-ions and VP nonsphericity configurational mean values distributions. The study shows that high concentrations favor a molten salt like structure while low concentrations tend to disrupt such ordering so small aggregates are more likely. The degree of separation between these forms is strongly determined by the charge of the ions. In the limit of low concentrations/high ionic charge, small clusters with some chainlike character are present which anticipates several features characteristic of the low density liquid-gas transition of the restricted primitive model. © 1994 American Institute of Physics.

## I. INTRODUCTION

The competition between the forces present in electrolyte solutions gives rise to a variety of structural features. Besides the usual short ranged repulsive and van der Waals interactions common to other fluids there are long ranged Coulombic forces and ion-solvent interactions. The Debye-Hückel and the ionic crystal are two well-known limiting cases which nevertheless cannot give an approximate idea of the structural richness of different electrolyte solutions as the concentration and ionic charge/solvent dielectric constant ratio are modified. Good examples of the assertion are the existence of electrolyte solutions that unmix to form two liquid phases<sup>1</sup> or the appearance of a low-density critical point in a classical fluid of charged hard spheres.<sup>2-4</sup> The concept of ion-pairing, introduced by Bjerrum<sup>5</sup> provided new insights into the behavior of these ionic systems but the association phenomena are much more complex than the simple model of neutral pairs. Fuoss and Kraus proposed the existence of trimers to explain electrical conductivity measurements.<sup>6</sup> More recently, the predictions of integral equation theories<sup>7</sup> and, especially, the analysis of computer simulations<sup>8-10</sup> have proven the presence of complex aggregates in moderately concentrated 2:2 electrolyte solutions.

The most widely used quantity in structural studies of liquids is the pair distribution function  $g(r)$ . This function gives only an averaged information about the system structure so the association is masked<sup>8</sup> and others methods are needed. Cluster analysis has proven to be a useful tool to this objective.<sup>8-11</sup> The requirement of a cluster condition to the pair distribution functions furnishes the so-called pair connectedness functions which have allowed a further progress in the knowledge of aggregation phenomena.<sup>12</sup> Nevertheless, both the cluster analysis and the pair connectedness functions rely on the use of a *predefined* distance as the criterion to consider two ions as part of the same cluster. The choice of the connectivity distance is not obvious and, more importantly, the clusters obtained involve only the closest ions within such distance. Little information is obtained about the positions of the ions beyond the distance defining the linking criterion (though the comparison of the results for different choices of the clustering variable throw some light on this

respect<sup>8,10,12</sup>). Hence, the interest of investigating structural properties sensitive not only to the two or three immediate ions but also to the global environment surrounding every ion. The Voronoi polyhedra (VP)<sup>13</sup> seem to fulfill the desired requirements.

The VP, defined as the convex region of space closer to its central particle than to any other, are a generalized version of the Wigner-Seitz cells common in crystallography. As long as VP reflect topological and metric properties of the environment of each particle, a study of these properties can provide a useful information on the arrangement of the ions in solution. This information is qualitatively different from that furnished by standard methods such as the pair correlation functions. Now the interest does not rely on how close is a neighbor particle but on whether or not it is the closer one in that direction.<sup>14</sup> The Voronoi polyhedra analysis was first employed by Bernal<sup>15</sup> to the case of a random packing system. Since then, it has been used as a tool in structural characterization in different fields such as crystallization,<sup>16-21</sup> glass formation,<sup>22,23</sup> water and solvation structure,<sup>24-26</sup> defects in melting transition,<sup>27,28</sup> solvolytic reactions,<sup>29</sup> molecular volumes of proteins,<sup>30,31</sup> and substrate-enzyme structures.<sup>32,33</sup> In a recent work,<sup>14</sup> we have shown that the properties of the VP can serve to identify the state of the system. Specifically, the study of the VP volumes distribution and its symmetry for two differently quenched Lennard-Jones liquids suggested several features as being characteristic of the presence of aggregates. In this article we analyze the Voronoi tessellation of computer simulated 1:1, 2:2, and 3:3 aqueous solutions in the low to very high concentration range. The objective is to provide new elements to the structural characterization of the ionic distribution and association phenomena.

## II. METHODOLOGY

The systems covered by this study are 1:1, 2:2 and 3:3 electrolyte solutions obtained via standard Monte Carlo simulation. The concentration range studied for the 2:2 systems varies from 0.0625 to 4 M, between 0.25 and 2 M for the 1:1 solution whereas the investigation of 3:3 electrolytes involves the study of just a point at 0.11 M. This allows to

appreciate the structural variations as a function of concentration, ionic charge and ionic strength. The interionic potentials are given by the expression<sup>11</sup>

$$u_{jj'}(r) = B[(\sigma_j + \sigma_{j'})/r]^{n_c} - e_j e_{j'} / \epsilon r, \quad (2.1)$$

where  $e_j$  is the charge and  $\sigma_j$  the nominal radius of ion  $j$ . The parameter  $n_c$  modifies the slope of the repulsive forces and  $\epsilon$ , the relative dielectric constant of the solvent, the strength of the Coulombic interactions. The coefficient  $B$  is defined as

$$B = A |z_j z_{j'}| e^2 / n_c (\sigma_j + \sigma_{j'}), \quad (2.2)$$

being  $A$  the ratio of the Madelung's constant to coordination number for the crystal,  $z_j$  the electrovalence of ion  $j$  and  $e$  is the electron charge. Minimum image convention is used together with periodic boundary conditions. Negligible differences have been observed from the results presented in this paper and the same calculations done for systems obtained by

Stochastic Dynamics using the Ewald summation method to account for the long range electrostatic interactions with the replicated boxes.<sup>10</sup> For all runs  $n_c = 9$ , and the ionic radii  $\sigma_+ = \sigma_- = 1.4214 \text{ \AA}$ . The sample consisted of 216 particles (108 anions and cations) at 298.16 K. For the highest concentration (4.0 M) a small dependence of the results on system size was observed. For this particular case, a 512 particle sample was used instead. The number of attempted single-particle moves in the production phase of the simulations was around 7 million from which over 500 configurations were used in the Voronoi polyhedra analysis.

The 3D Voronoi polyhedra (VP) construction is a non-trivial problem for which a few algorithms have been proposed. When the particles have not a solidlike structure the system is usually ill-conditioned and algorithms based on the use of a cutoff radius to locate the closest neighbors are prone to error. In this work we use an algorithm specially devised to deal with disordered systems.<sup>14</sup> Both the algorithm and the results for different properties of the tessellation were tested in the case of simple Lennard-Jones (LJ) systems (corresponding to the gas, liquid, quenched liquid, and solid states). Although a description of the method does not proceed here (the interested reader can find it in Ref. 14) it is worth noting some points. The algorithm is robust in the sense that it always provides a solution to the problem. The method is approximate but the accuracy of the tessellation can be easily monitored through the sum of the Voronoi polyhedra volumes. Although the sum of the VP volumes for any configuration should match the simulation cell volume  $V_{\text{cell}}$ , approximate Voronoi constructions have always (in our method) volumes equal or bigger than the true one; the difference between the total VP and cell volumes is therefore a measure of the accuracy of the tessellation. Our experience is that an error of 0.1% in the total volume gives completely satisfactory results for all the properties of the polyhedra studied.

### III. RESULTS

The Voronoi tessellation leads to a partition of the space which allows to (unambiguously) assign a volume to every

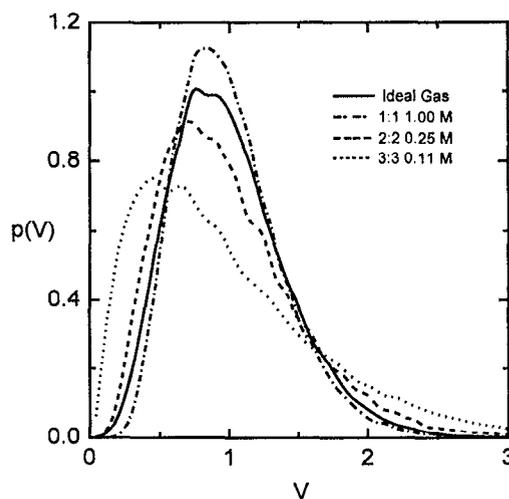


FIG. 1. Distribution of Voronoi polyhedra volumes for systems at the same ionic strength. The ideal gas results are also depicted for comparison.

ion. Then the distribution properties of the Voronoi polyhedra volumes  $p(V)$  are a reflect of the the interparticle potential effects. Figure 1 displays the distributions  $p(V)$  of VP volumes for three systems at the same ionic strength. Volumes are reduced with the mean space available for each particle— $V_{\text{cell}}/N_{\text{ions}}$ —and the distributions have been normalized so that

$$\int_0^{\infty} p(V) dV = 1. \quad (3.1)$$

The results for a system of noninteracting particles—the ideal gas values  $p(V_{\text{i.g.}})$ —have also been depicted. Highly charged (2:2 and 3:3) electrolytes and 1:1 solutions show a distinct behavior, especially when compared against the non-interacting system. The curves of the two latter systems exhibit similar trends, namely, sharpened and rather symmetric distributions. The only remarkable difference between them lies in the height of the peak which is higher in the electrolyte than in the ideal gas. On the contrary, the curves for solutions involving highly charged ions are more flat and significantly asymmetric. The asymmetry has its origin in the existence of aggregates. The inner particles of such clusters have very small VP volumes while other particles are left more or less isolated thus exhibiting large Voronoi polyhedra. In fact, as the charge increases, the shape of the curves—a steep slope at small volumes followed by a slow decay—approaches that of a heavily quenched Lennard-Jones fluid.<sup>14</sup> A measurement of the asymmetry of a distribution is provided by the so-called skewness coefficient  $m_{3/2}$  defined as

$$m_{3/2} = M_3 / M_2^{3/2}, \quad (3.2)$$

where  $M_n$  is the  $n$ th moment about the mean value of the distribution. The numerical results are shown in Table I.

A more thorough discussion of those results will be given below. Here, we would like to pay some attention only to the value for the 3:3 electrolyte—1.17—which is very

TABLE I. Skewness coefficients  $m_{3/2}$  of the VP volume distributions and mean values of the quotient of surfaces shared with unlike- and like-ions  $\langle S_u/S_l \rangle$ .

System	Concentration/ $M$	$m_{3/2}$	$\langle S_u/S_l \rangle$
Ideal gas	...	0.74	1.01
1:1	2	0.77	1.43
	1	0.81	1.39
	0.5	0.81	1.34
	0.25	0.80	1.30
	0.125	0.78	1.30
2:2	4	0.68	
	2	0.86	1.84
	1	0.97	1.79
	0.5	1.01	1.74
	0.25	1.04	1.70
	0.125	1.00	1.16
0.0625	1.13	1.16	
3:3	0.11	1.17	1.16

close to that of a quenched LJ liquid—1.18. This is an indication of the strong degree of association present in that system. The results of Fig. 1 deserve a final comment regarding the type of aggregates one would find in dilute solutions of highly charged ions. *True* ion-pairs, i.e., two close ions far away from the rest of the particles, would behave as a single noncharged particle so it is to be expected that their combined VP volume should be close to the mean space available to the particles  $V=1$ . Thus, each of the two ions forming a pair should have VP volumes slightly above  $1/2$ . Because of the great number of ions with volumes smaller than  $1/2$ , the distribution obtained for the 3:3 electrolyte give support to the existence of structures more complex than just pairs. This is reasonable if one realizes that this point is close to a low-density critical region.<sup>2-4</sup>

In Fig. 2 we compare the VP volume distributions for 1:1 and 2:2 electrolytes at several concentrations. Besides, to isolate the effect of the interionic forces, the results for the ideal gas system  $p(V_{i.g.})$  have been subtracted out. The first minimum in the curves for the more concentrated solutions is brought about by the repulsive forces which make very unlikely the existence of close neighbors. It is quite deep at concentrations over  $1 M$  meaning that the short-range forces play an important role in the structure at these concentrations. Other features of the upper plots in Fig. 2 which are also due to the repulsion between the electronic cores are the maximum at  $V=1$  (the mean available volume) and the relative absence of isolated ions denoted by the minimum beyond  $V=1.5$ . As packing considerations apply both to 1:1 and 2:2 electrolytes, the distributions of VP volumes are similar at high concentrations despite the differences in their Coulombic forces. The overall appearance of  $p(V)$  for solutions whose structures are determined by repulsive interactions were shown in Fig. 1. There we noted the symmetry of the curves which can be tracked through the skewness coefficient of the VP volume distributions  $m_{2/3}$ . In Fig. 3 we compare the  $m_{2/3}$  values of the electrolyte solutions with those of the ideal gas, a representative Lennard-Jones liquid

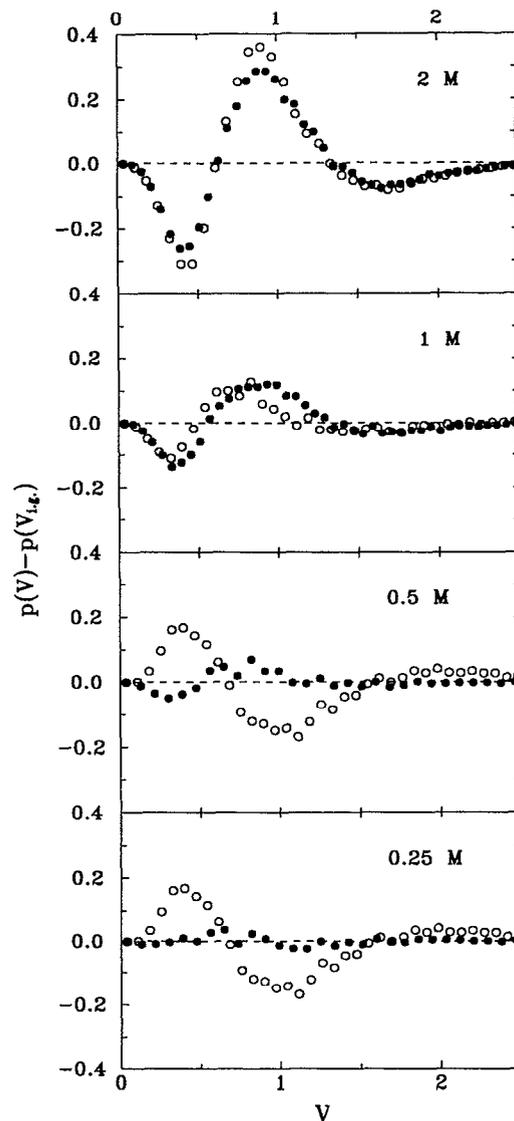


FIG. 2. Distribution of Voronoi polyhedra volumes relative to the ideal gas results. (●) 1:1 aqueous solutions at several concentrations; (○), 2:2 electrolytes.

and a quenched system obtained from that liquid (see Ref. 14). At concentrations above  $1 M$ , the skewness coefficient of both 1:1 and 2:2 electrolytes slip in the ideal gas zone approaching that of a LJ liquid (and, eventually, a solid LJ result). The type of aggregation in this high concentration regime is thus completely different to that found in the 3:3 electrolyte. Now, each ion in the solution has a similar environment as every other.

The repulsive effects in the VP volume distribution are less important below  $1 M$  and vanish at concentrations about  $0.25 M$ . This fact makes evident the strong structural differences between 1:1 and 2:2 aqueous solutions. The weak electrostatic interactions are completely unable to induce a substantial ordering in the former system so the departures of the  $p(V)$  curves respect to the ideal gas become flat (Fig. 2). In this sense, the structure of 1:1 electrolytes depends on

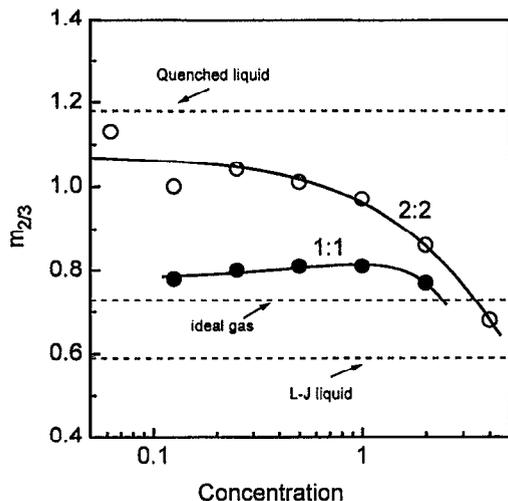


FIG. 3. Skewness coefficient [see Eq. (3.2)] of the VP volume distribution for 1:1 (●) and 2:2 (○) electrolytes. Dashed lines are the coefficients for several representative systems (Ref. 14).

concentration in a similar way as a gas does. The similarities are even greater when it is realized that also the skewness coefficients are, at any concentration, only slightly above that of the ideal gas (Fig. 3).

The case of highly charged electrolytes is completely different. We have already seen that the VP volume distributions at the highest concentrations of this study are essentially dependent of the repulsive forces so the structures of 1:1 and 2:2 electrolytes appear quite similar. When packing effects are less important, a short-range ordering produced by the strong electrostatic interactions emerge. It can be seen in Fig. 2 that, at concentrations lower than 0.5 M, the  $p(V) - p(V_{i,g})$  curves develop *new* maxima and minima while those characteristic of the ionic packing blur. As commented above, the first peak in the 2:2 electrolyte plots can be ascribed to the existence of ionic aggregates: since the Coulombic interactions hold some ions together, its corresponding VP volumes decrease. It is to be stressed that the distribution exhibits a minimum just for the average volume  $V=1$ . As the concentration decreases the 2:2 electrolyte curves also exhibit a broad maximum at high volumes. Despite the height of this peak the corresponding ions hold a substantial part of the total volume. This means—schematically—that the ions in relatively dilute solutions made of highly charged particles are either closely surrounded by other ions (forming clusters) or isolated. The results for  $m_{2/3}$  also support this idea. It can be seen in Fig. 3 how the  $p(V)$  skewness coefficients approach that of a quenched LJ liquid. Thus,  $m_{2/3}$  reveal that highly charged electrolytes exhibit two completely different types of aggregation in the high-density limit (molten salt like structure) and low-concentration one (quenched like aggregates), respectively. In Fig. 4 we represent the fraction of ions  $N(v)$  with VP volumes smaller than  $v$  and the fraction of the total volume occupied by these ions  $V_f(v)$

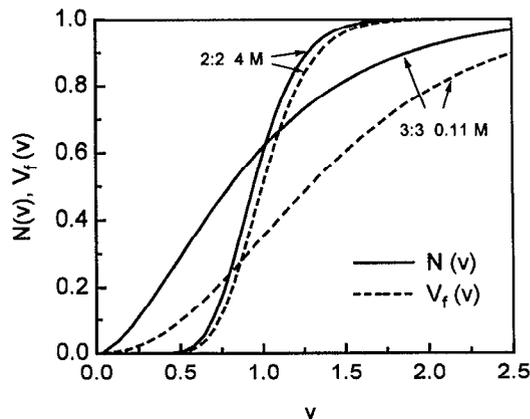


FIG. 4. Fraction of ions  $N(v)$  with VP volumes smaller than  $v$  and fraction of the total volume occupied by these ions  $V_f(v)$  for two representative cases of electrolytes with extremely different structures.

$$N(v) = \int_0^v p(v') dv', \quad (3.3)$$

$$V_f(v) = \int_0^v v' p(v') dv', \quad (3.4)$$

for two states representative of these extreme cases, namely 2:2 electrolyte at 4 M concentration and 3:3 0.11 M. In the concentrated solution, both curves are almost coincident indicating once again that each ion has almost the same environment as every other while the ions in the dilute one are either in clusters or rather isolated—the  $V_f(v)$  curve comes apart from that of  $N(v)$  at the smaller volumes, the departure only disappearing at high  $v$ .

The distribution of volumes informs about the space available to the particles but cannot tell whether the Voronoi neighbors are like- or unlike-charged ions. It should be easy to obtain the mean number of neighbors of each kind, but two important drawbacks<sup>14</sup> make such procedure irrelevant to our purposes. The shortcomings are the discreteness of the distribution (several differently structured systems have a mean number of neighbors close to 14) and, secondly, the fact that the same weight is given to a big face (shared between two very close neighbors) and to a small one (for instance, a small cut in a vertex produced by a particle which is much farther away). The latter point suggest a measure of how preferentially unlike ions surround a given particle. As long as close neighbors tend to produce big faces, the surface of the VP faces shared with unlike ions,  $S_u$ , divided by that shared with the like charged ones,  $S_l$ , gives an idea of the distribution of the different kinds of ions around a target one. The configurational averages are shown in Table I. In general, the quotient decreases with concentration. The variation is smooth in the case of 1:1 electrolytes with values indicating that unlike ions are a little bit closer than like ones. The same holds for concentrated solutions of 2:2 aqueous solutions, but the results are now significantly higher revealing that the structure is enhanced by stronger electrostatic interactions. There is an abrupt drop at concentrations about

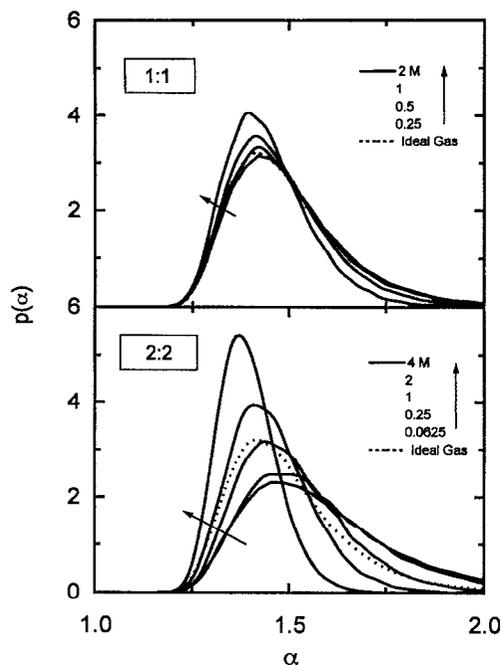


FIG. 5. Distribution of the Voronoi polyhedra nonsphericity parameters. Upper plot, 1:1 electrolytes; lower plot, 2:2.

0.125 *M*. Numerical errors (which we estimate to be well below  $\pm 0.05$ ) cannot be invoked to account for such sudden change. In fact, we have made another evaluation of this property for the 0.125 *M* system with a completely independent simulation code (Brownian Dynamics and Ewald sums<sup>8</sup>) obtaining the same result. The change in  $\langle S_u/S_l \rangle$  should correspond to the transition between the molten-salt type structure to the quenched like one. For the latter structure, the ions belonging to the aggregates have small volumes and, thus, surfaces. In this way, the quotient for the whole system rely essentially on that of the isolated ions whose value must be close to unity. Although such argument would be an explanation for lower values of  $\langle S_u/S_l \rangle$  at decreasing concentrations, the question which would remain unassessed is why the drop is so dramatic at concentrations below 0.25 *M* in 2:2 electrolytes.

A suitable parameter to define the shape of a convex body (Voronoi polyhedra are indeed convex bodies) is the so-called nonsphericity, also referred to as anisotropic factor  $\alpha$ . It is defined by

$$\alpha = \frac{RS}{3V}, \quad (3.5)$$

$V$ ,  $S$ , and  $R$  being the volume, surface, and average curvature radius of the convex body, respectively. This parameter is the unity for a sphere and increases with the anisotropy of the geometric object; for a representative LJ liquid the distribution of this property has a maximum about 1.3.<sup>14</sup> For the evaluation of the nonsphericity parameter  $\alpha$ , the mean curvature radius,  $R$ , of the corresponding convex body must be known. For a polyhedron,  $R$  is given by<sup>34</sup>

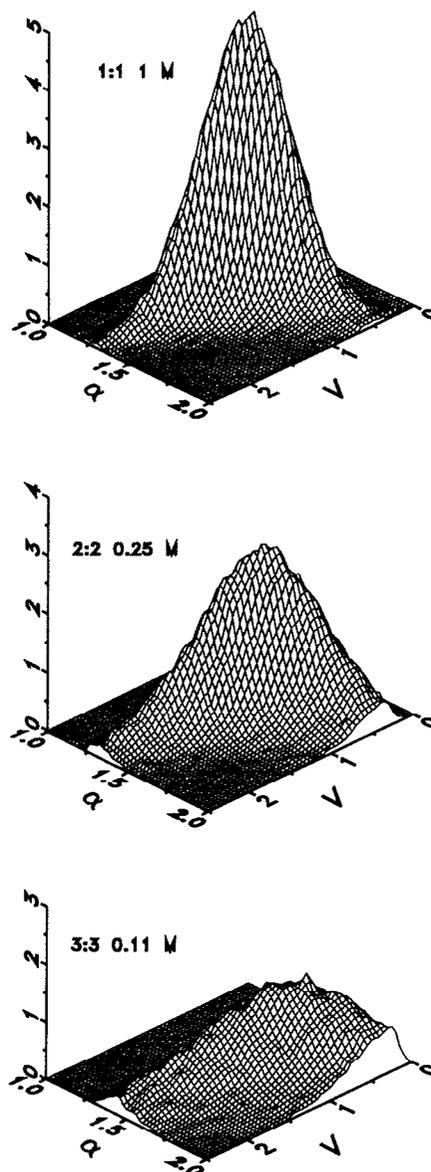


FIG. 6. Bivariate distribution of VP volume-anisotropic factor for systems with the same ionic strength.

$$R = \frac{1}{8\pi} \sum l_i \phi_i. \quad (3.6)$$

The sum extends over polyhedron edges of length  $l_i$  and  $\phi_i$  is the angle between the normal vectors to the intersecting faces. The nonsphericity distributions for all the systems studied are shown in Fig. 5. Irrespectively of the ionic charge, at high concentrations the distributions exhibit peaks for values of  $\alpha$  close to that of the LJ liquid. This means that the ionic environment is more or less spherical. At 1 *M* concentration, the distribution are almost identical for both types of electrolytes. When moving towards lower concentrations, we found again a distinct behavior for each type. As 1:1 electrolytes become more diluted the distribution of VP nonsphericities move to that of the ideal gas whereas 2:2 solu-

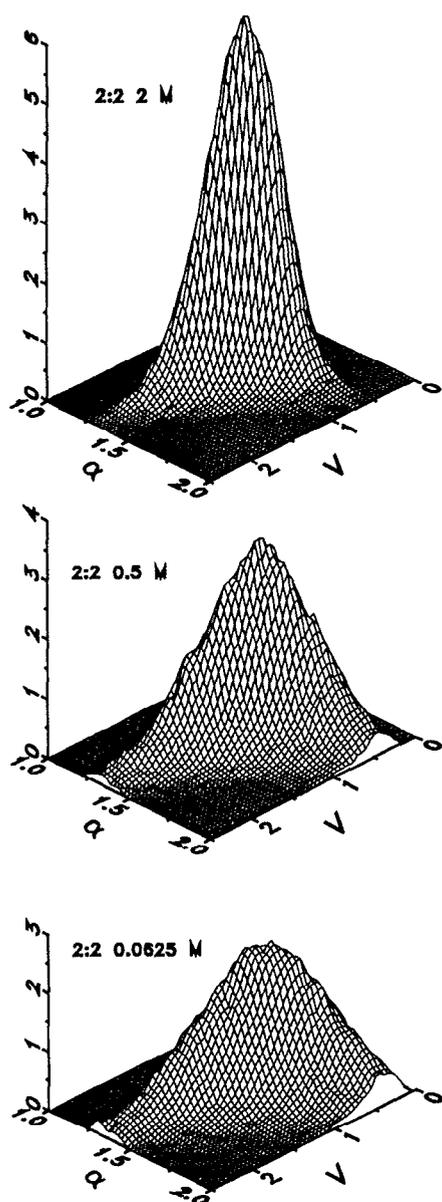


FIG. 7. Same as Fig. 6, but for 2:2 systems.

tions do not. In the latter case, the peaks shift toward higher  $\alpha$  and values as high as 1.8 (roughly the anisotropic factor of a prism with edges ratio 1:2.5:2.5) are not rare.

The statistical quality of the results allows the calculation of volume-anisotropic factor cross distributions. Leaving aside the more or less sharpened character of the curves (which was already discussed in the preceding paragraphs) the more striking features of such 3D plots (Figs. 6 and 7) are the appearance of *arms*. The constant probability contour plots have a boomerang like shape. Figure 8—the contour plot for the 2:2 0.25 M system—serves to illustrate this point and to show the general aspect of the 3D drawings (especially the hidden parts of Figs. 6 and 7) as well. The arms develop along regions of either low  $\alpha$  or  $V$ , i.e., most of the highly nonspherical Voronoi polyhedra have small volumes while the majority of the bigger VP exhibit low anisotropic factors.

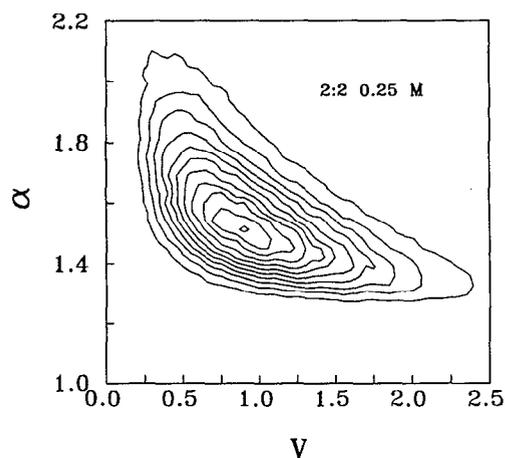


FIG. 8. Constant probability contour plot of the VP distribution as a function of volume and nonsphericity parameter for the 2:2 0.25 M solution.

It is easy to ascribe those extreme cases to ions taking part of aggregates and to isolated ions, respectively. Thus, the more developed the arms the more likely the existence of ionic aggregates. From this point of view, Figs. 6 and 7 would add little to previous conclusions. Nevertheless, there is a point which deserves some attention. If the aggregates were compact, the inner ions of the clusters would see a (more or less) spherical environment; only the superficial ones might exhibit high anisotropic factors. But the 3D plots show that the *smaller* VP have a *strongly non-spherical* environment revealing that the cluster structures contain a majority of superficial ions. Figure 6, depicting the results for systems with the same ionic strength, shows that these noncompact structures are very important in highly charged/low concentrated solutions. In other words, the disruption of the molten salt structure proceeds through the formation of aggregates with some chainlike character. This conclusion was already suggested by a cluster analysis of electrolyte solutions.<sup>8</sup> Moreover, snapshots of the restrictive primitive model in the vicinity of the low density transition actually exhibit a chainlike ordering.<sup>35</sup>

In view of the discussions of the preceding paragraphs, it seems coherent that the arms fade away as the concentration increases in 2:2 electrolytes (Fig. 7). As expected, the plots for 1:1 aqueous solutions are all quite similar (and close to the 2:2 1 M distribution). For this reason we have not depicted such calculations.

#### IV. FINAL REMARKS

In this paper we have presented a Voronoi polyhedra analysis of the structure of electrolyte solutions. Although the theoretical support of the VP analysis needs to be more thoroughly understood, we show that several magnitudes associated with the distribution of VP volumes and shapes are able to throw light about the structural variations as the ionic charge or concentration are changed. Thus, the first main conclusion of this paper is the confirmation of the VP technique as a powerful tool in structural analysis. On the other hand, concerning the structure of electrolyte solutions, our

study shows that high concentrations favor a molten salt like structure and low concentrations tend to disrupt such ordering so small aggregates are more likely. The degree of separation between these forms is strongly determined by the charge of the ions. Indeed, the results for the 3:3 0.11 M systems announces in some way the vicinity of the low-density phase transition. The conclusions are similar as those obtained by means of a cluster analysis<sup>8,10</sup> or through the pair-connectedness functions.<sup>12</sup> Given the important differences between these techniques, this fact reinforces our picture of the structure of electrolyte solutions.

#### ACKNOWLEDGMENT

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<sup>1</sup>H. L. Friedman, *J. Phys. Chem.* **66**, 1595 (1962).

<sup>2</sup>G. Stell, K. C. Wu, and B. Larsen, *Phys. Rev. Lett.* **37**, 1369 (1976).

<sup>3</sup>G. Orkoulas and A. Z. Panagiotopoulos, *J. Chem. Phys.* **101**, 1452 (1994).

<sup>4</sup>J. M. Caillol, *J. Chem. Phys.* **100**, 2161 (1994).

<sup>5</sup>N. Bjerrum, *Kgl. Danske Videnskab. Selskab Mat. Fys. Medd.* **7**, 9 (1926).

<sup>6</sup>R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.* **55**, 2387 (1933).

<sup>7</sup>H. L. Friedman and B. Larsen, *J. Chem. Phys.* **70**, 92 (1979).

<sup>8</sup>J. L. F. Abascal and P. Turq, *Chem. Phys.* **153**, 79 (1991).

<sup>9</sup>D. E. Smith, Y. V. Kalyuzhnyi, and A. D. J. Haymet, *J. Chem. Phys.* **95**, 9165 (1991).

<sup>10</sup>J. L. F. Abascal, F. Bresme, and P. Turq, *Mol. Phys.* **81**, 143 (1994).

<sup>11</sup>P. J. Rossky, J. B. Dudowicz, B. L. Tempe, and H. L. Friedman, *J. Chem. Phys.* **73**, 3372 (1980).

<sup>12</sup>F. Bresme and J. L. F. Abascal, *J. Chem. Phys.* **99**, 9037 (1993).

<sup>13</sup>G. Voronoi, *Z. Reine Angew. Math.* **134**, 199 (1908).

<sup>14</sup>J. C. Gil Montoro and J. L. F. Abascal, *J. Phys. Chem.* **27**, 4211 (1993).

<sup>15</sup>J. D. Bernal, *Proc. R. Soc. London, A* **280**, 299 (1964).

<sup>16</sup>M. Tanemura, Y. Hiwarati, H. Matsuda, T. Ogawa, N. Ogita, and A. Ueda, *Prog. Theor. Phys.* **58**, 1079 (1977).

<sup>17</sup>C. S. Hsu and A. Rahman, *J. Chem. Phys.* **70**, 5234 (1979).

<sup>18</sup>J. N. Cape, J. L. Finney, and L. V. Woodcock, *J. Chem. Phys.* **75**, 2366 (1981).

<sup>19</sup>S. Nose and F. Yonezawa, *J. Chem. Phys.* **84**, 1803 (1986).

<sup>20</sup>T. Z. Hsu and C. Y. Mou, *Mol. Phys.* **75**, 1329 (1992).

<sup>21</sup>M. J. Uttomark, M. O. Thompson, L. A. Báez, and P. Clancy, *Molec. Sim.* **11**, 121 (1993).

<sup>22</sup>M. Tanaka, *J. Phys. Soc. Jpn.* **55**, 3108 (1986).

<sup>23</sup>M. S. Watanabe and K. Tsumuraya, *J. Chem. Phys.* **87**, 4891 (1987).

<sup>24</sup>E. E. David and C. W. David, *J. Chem. Phys.* **78**, 1459 (1983).

<sup>25</sup>G. Ruocco, M. Sampoli, and R. Vallauri, *J. Chem. Phys.* **96**, 3857 (1992).

<sup>26</sup>J. P. Shih, S. Y. Sheu, and C. Y. Mou, *J. Chem. Phys.* **100**, 2202 (1994).

<sup>27</sup>M. P. Allen, D. Frenkel, W. Gignac, and J. P. McTague, *J. Chem. Phys.* **78**, 4206 (1983).

<sup>28</sup>A. Baranyai and I. Ruff, *J. Chem. Phys.* **85**, 365 (1986).

<sup>29</sup>V. Bellagamba, R. Ercoli, A. Gamba, and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1127 (1986).

<sup>30</sup>F. M. Richards, *J. Mol. Biol.* **82**, 1 (1974).

<sup>31</sup>B. J. Gellatly and J. L. Finney, *J. Mol. Biol.* **161**, 305 (1982).

<sup>32</sup>C. W. David, *Biopolymers* **27**, 339 (1988).

<sup>33</sup>R. A. Lewis, *J. Comput. Aided Mol. Design* **3**, 133 (1989).

<sup>34</sup>H. Hadwiger, *Altes und Neues über konvexe Körper* (Birkhäuser Verlag, Basel, 1955).

<sup>35</sup>F. Bresme, E. Lomba, J.-J. Weis, and J. L. F. Abascal, *Phys. Rev. E* (in press).