Molecular simulations of concentrated aqueous solutions: Ionic equilibrium structures in solutions

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ABSTRACT

The computer simulation methods have been applied to study the structure of aqueous solutions of simple ionic salts in the region of very high concentrations. The calculations of ionic structures in solutions were performed for NaOH, NaCl, LiCl and $MgCl_2$ solutions. The concentrations ranged from 0.2 M to saturated solutions, in some cases as much as 19 M.

A particularly careful analysis was devoted to the topology of the ionic structures in solution. Up to now, most of the research on ionic solutions was devoted to studies of the ionic hydration shells. However, beyond the Debye – Huckel range of very low concentrations, very little is known about the interionic spatial correlations. Certain theories predict the existence of ionic quasi-lattices in the region of high concentrations.

In the present work we used the Molecular Dynamics method combined with such statistical tools as the radial distribution functions, Voronoi tessellations, the running and O'Keeffe coordination numbers, *etc.*, in order to analyze the ionic structures. The radial distribution functions of three types: the cation – anion, cation – cation and the anion – anion type were calculated for each solution. The functions are typical for the quasi-crystalline order within the first 2 – 3 ionic coordination layers around a selected ion. The order is particularly pronounced for the anion – cation RDF's.

The distributions of the sphericity factor of the Voronoi polyhedra were calculated for the ionic substructures in the configurations produced by the Molecular Dynamics simulation. The increase of the ion concentration causes evolution of these distributions towards increased signatures of predominant geometries of the Voronoi polyhedra. This, together with the results for RDF's, provides a strong conjecture for existence of the ordered structures of ions in concentrated solutions.

Keywords: ionic solutions, lattice theory, computer simulation.

1. INTRODUCTION

The structure of ionic solutions - both the local structure of the solvation layers around the ions and the topology of the ion distributions in solution - is of primary importance for our understanding of nucleation phenomena and growth of crystals from the solutions. Unfortunately the aqueous solutions of electrolytes represent a complicated case and can not be described by any analytical theory in the full range of concentrations. For low concentrations of ions there is a number of theoretical models that work reasonably well: among others the Debye-Hückel theory, the hyper-netted chain theory, the mean spherical theory (see [1, 2] for references). All these theories converge to the same result - the limiting laws of the Debye-Hückel theory - when the ion concentration decreases to zero. On the other hand, at the range of high concentrations the validity of the models deteriorates very quickly and another theory should be introduced. Such a theory, based on the lattice-like topology of the ionic structures, has been mentioned and discussed many times in the literature. The consequent formulation of the theory has been provided by Frank and Thompson [3]. The most complete version of the lattice theory of concentrated electrolytes was given in a series of papers by Ruff and coworkers [4, 5, 6]. The model proposed by Ruff is can be

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described as follows. **(1)** The ions are distributed in a lattice - like arrangement. The positions of the ions are allowed to deviate randomly from the lattice sites. **(2)** The ions are immersed in a structureless continuous dielectric and their coulombic interactions are scaled down with the average dielectric constant which may be taken as a function of interionic separation distance. The medium around the ions has a dielectric gradient which acts as a repulsive force between the ions at short separation distances.

Comparisons of calculated and observed data for the dielectric constant, activity coefficients and partial molar enthalpy of several 1-1 and 1-2 electrolytes show fairly good agreement in entire concentration range [4,5]. It has been shown [6] that in the limit of dilute systems, the deviations of the ion distribution from the lattice positions grow and the lattice theory converges to the Debye-Hückel theory.

In the modern investigations of liquids and liquid solutions the computer experiments play the important role occupying in a way an intermediate place between theory and experiment. In the case of very complicated problems, that are impossible to treat in an analytical way, the simulations correspond to the theory. On the other hand, for simpler and more tractable problems, the simulations can be used as a check against existing analytical theories. Hence, we propose to check the lattice theory of concentrated strong electrolytes by comparing it with the results of the computer experiment for these media.

The computer simulation method has been frequently used, with remarkable success, to predict the structure and physico-chemical properties of aqueous electrolyte solutions. The first simulations were performed by Heinzinger as early as 1974. We refer to the review papers [7,8] as the source of references. However, with very few exceptions like *e.g.* [9], most of the calculations concerned the solvation structures of the ions, that is the geometrical arrangements of water molecules in the vicinity of the cations and anions. The ion - ion correlations were either neglected or shown by the radial correlation functions. The investigation of the geometry of the ion arrangements is very difficult. In order to obtain reliable results one has to include in the simulation box at least a hundred of ions and proportional number of water molecules that results from relative concentrations. This increases the quantity of atomic objects in the simulation box to almost intractable number and such calculations have become possible only recently due to the increase of the speed of available computers.

2. COMPUTER SIMULATION METHOD

2.1. Simulation details.

The simulations have been performed by the Molecular Dynamics method [10] using the flexible model of water. The box contained 400-2000 water molecules and the number of ions that results from the concentration of the solution and the size of the box (16-160 ions). The simulation box was assumed in the cubic form with the size ranging between 2.5 and 4.1 nm, depending on the ion concentration. The calculations were performed for NaCl and $MgCl_2$ solutions with concentrations ranging from 0.2 to about 5.0M as well as for LiCl and NaOH solutions with concentrations from 0.5 to 19.0M.

The ion-ion interaction was assumed as a sum of the Coulomb potential and the Lennard-Jones interactions. The interaction parameters were taken from the Universal Force Field version 1.02 and the shifted force method for non-coulombic interactions has been applied. The periodic boundary conditions have been employed with the Ewald summation for calculations of the long-range electrostatic forces. A typical simulation run included three stages: (a) the initial, equilibration phase of $1 \div 2 \times 10^4$ time steps with the temperature scaling, (b) the control phase of 1×10^4 time steps and (c) the proper simulation of $4 \div 8.5 \times 10^4$ time steps. The elapsed time of the proper simulation reached 40÷85 ps and the temperature oscillated near 300 K. The analysis of the ionic structures was performed using the radial distribution functions (RDF) and stochastic Voronoi polyhedra.

2.2. Analysis of radial distribution functions and Voronoi polyhedra.

The local structure of a disordered medium can be described by a set of distribution functions for atomic positions. The pair distribution function $g_2(r_i, r_j)$ (usualy calculated as a function $g(r)$ of radial distance only and called the radial distribution function, RDF) is most often used. The value of $g(r)$ at a given r represents the density of probability of finding

a pair of atoms separated by the distance r relative to the probability expected for an uniform distribution of atoms with the same density. The formula for calculating $g(r)$ is given by:

$$g(r) = (V/N)^2 \; < \Sigma\Sigma_{ij,\, i \neq j} \, \delta(r - r_{ij}) > \qquad (1)$$

where N is the number of particles in volume V, δ denotes the Dirac delta, the brackets < > denote the averaging over the ensemble of the particles, the sums over i and j run over the different pairs of the particles in the simulation box.

For a multicomponent system the radial distribution function can be defined for each type of the atom pair. For an AB mixture the following functions : g_{AA}, g_{AB}, g_{BB} can be defined. In the present paper we calculate the RDF's describing spatial correlations between ions: the cation – anion RDF, cation – cation RDF and anion – anion RDF. It is commonly assumed [10] that the region of the distances from 0 through the first maximum up to the first minimum of the RDF corresponds to the first neighbourhood of the central atom, the region from the first minimum to the second minimum corresponds to the second neighbours, etc. The integrals of the RDF within the limits given above correspond to the number of the nearest neighbours of the central atom, the second nearest neighbours, *etc.*

Stochastic Voronoi polyhedra seem to be a very convenient tool for the description of the long range order in disordered systems [11]. The definition of the Voronoi polyhedron is illustrated in Figure 1. For a selected atom, referred to as the "central atom", we define the Voronoi polygon as the set of the points that are closer to the "central atom" than to any of the "medium atoms" of the disordered system. To find the Voronoi polygon we join the "central atom" and all the "medium atoms", then at the points halving the distances we draw perpendicular planes and select the minimal convex polyhedron constructed from these planes. Thus, the Voronoi polyhedron can be considered as a generalization of the well-known Wigner - Seitz symmetric cells to the disordered systems.

In an ideal crystal all the Voronoi polyhedra are identical and take on highly symmetrical forms. When the ion positions deviate from the lattice sites we observe rapidly increasing variety of the shapes of the Voronoi polyhedra. Some of the polyhedra acquire or loose one or more faces. Thus, we can construct the distribution of the number of faces of the Voronoi polyhedra drawn for the disordered set of points. The sets that are close to the crystalline order exhibit the distributions that are sharply peaked around the number of faces predominating in the system. In the limiting case of the perfect crystal, the distribution is a Dirac delta function placed at the number of faces which corresponds to the number of the first neighbours in the crystal lattice.

Figure 1 shows the Voronoi polyhedra plotted for a series of cubic lattices with the increasing random deviations of the atom positions from the lattice sites. The left upper part shows the polyhedron for an ideal lattice. The upper right part of the figure shows a typical polyhedron for the cubic lattice when atoms are allowed 20 % deviation from the lattice sites. The lower right part. shows a typical polyhedron drawn for one of the configurations obtained in the course of simulation of 13 M LiCl solution. It is worth noting that the upper right and lower right polyhedron are very similar one to another. These polyhedrons can be compared with the polyhedron of the lower left part of the Figure drawn for completely random set of points. We observed that even minor deviations from the ideal lattice, of the order of 1%, produce polyhedrons with a wide range of the shapes. The distributions for the distorted crystals are however clearly different than the distribution for the random system.

It was demonstrated that analysis of non-sphericity (or anisotropy) factor of the Voronoi polyhedra is suitable to the study of the structure of disordered systems. The anisotropy parameter is given by:

$$\alpha = \frac{A^3}{36\pi V^2} \qquad (2)$$

where A and V are the surface and volume of the Voronoi polyhedron. For a sphere α equals to 1, for the bcc, fcc and simple cubic lattices it equals to 1.33, 1.35 and 1.91, respectively. In limiting case of the perfect crystal, the distribution of α is the delta Dirac function. The sets of points that are close to the crystalline order exhibit sharply peaked distribution. For less-ordered systems the distribution is much broader and exhibits a bell-shaped form. The distributions of the anisotropy factors of the Voronoi polyhedra were calculated for the NaOH and $MgCl_2$ solutions with different concentrations. The distributions are shown in Figure 6 together with the distribution for a random set of points.

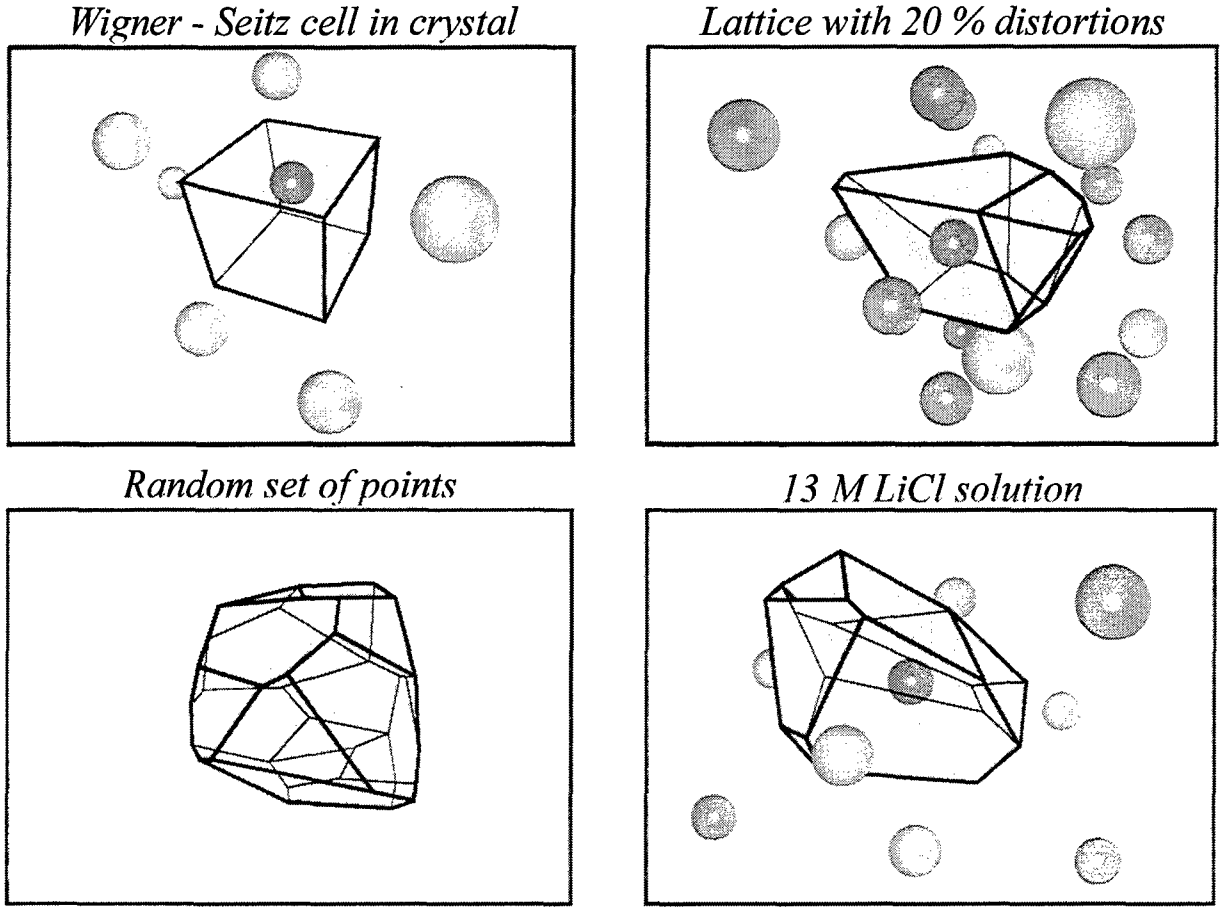

Fig.1. Voronoi polyhedra plotted for a series of systems with increasing random deviations of the atom positions from the lattice sites. The left upper part: the polyhedron (Wigner-Seitz cell) for an ideal cubic lattice. The upper right part: a typical polyhedron for the cubic lattice when atoms are allowed 20 % deviation from the lattice sites. The lower right part: shows a typical polyhedron drawn for one of the configurations obtained in the course of simulation of 13 M LiCl solution. The lower left part: a polyhedron drawn for random set of points.

3.RESULTS AND DISCUSSION

3.1. Radial distribution functions

The ion – ion pair distribution functions are plotted in the following arrangement: Figure 2 corresponds to NaOH solutions with concentrations 0.5 M, 3.0 M, 6.0 M and 19.0 M; Figure 3 to NaCl solutions with concentrations 0.3 M, 0.9 M, 2.8 M and 5.1 M; Figure 4 to LiCl solutions with concentrations 0.5 M, 5.0 M, 11.9 M and 14.0 M; Figure 5 to $MgCl_2$ solutions with concentrations 0.2 M, 1.1 M, 2.4 M and 4.9 M. The highest concentrations of the series are close to the saturation point. Each figure is composed of the upper, middle and lower part representing the cation – anion distributions, the cation – cation distributions and the anion – anion distributions, respectively. The distributions are additionally labeled in the figures.

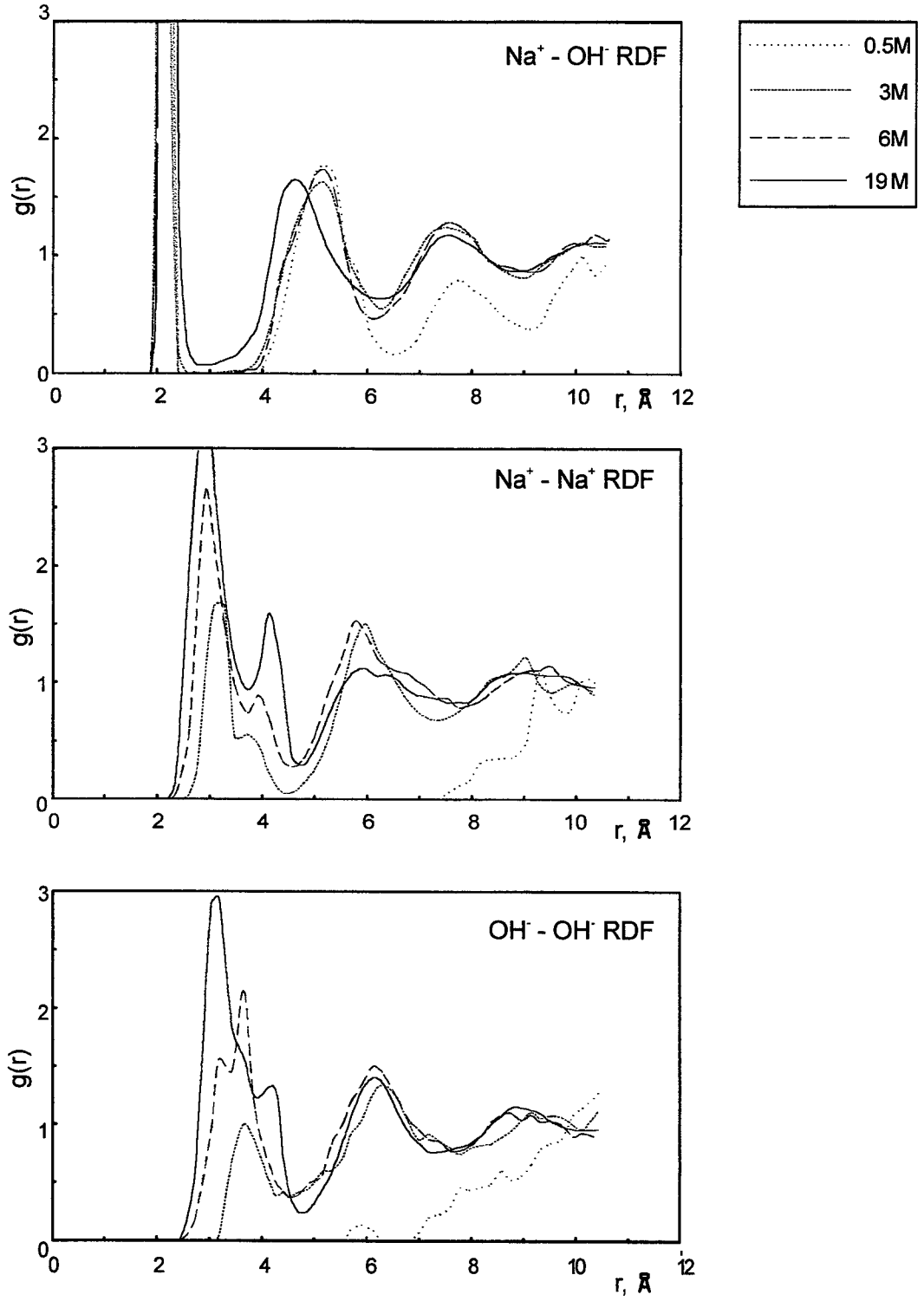

Fig.2. The ion – ion radial distribution functions for NaOH solutions with concentrations: 0.5 M, 3 M, 6 M and 19 M. The upper figure shows the Na^+ - OH^- RDF, the figure in the middle shows the Na^+ - Na^+ RDF and the lower figure shows the OH^- - OH^- RDF.

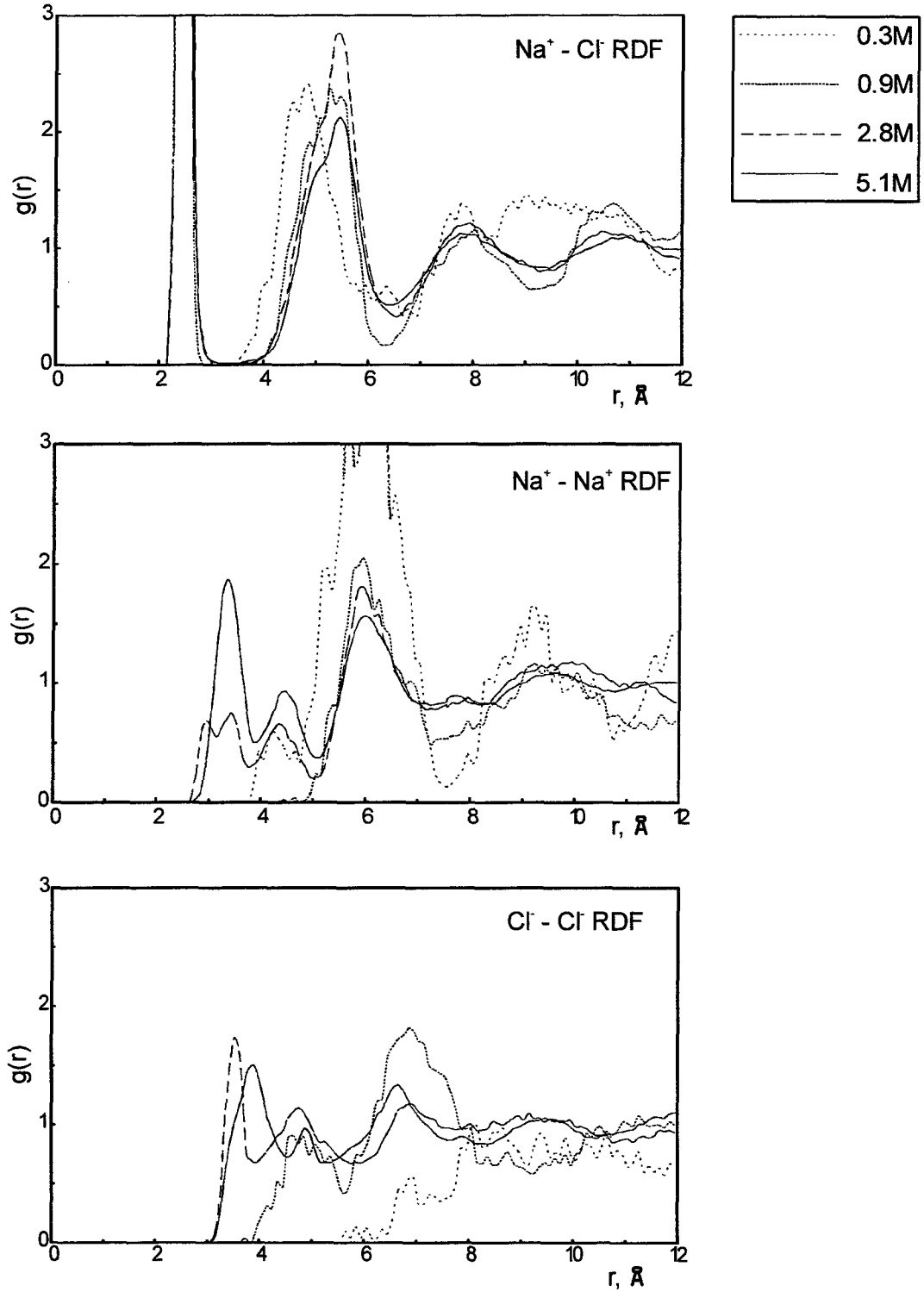

Fig.3. The ion – ion radial distribution functions for NaCl solutions with concentrations: 0.3 M, 0.9 M, 2.8 M and 5.1 M. The upper figure shows the Na^+ - Cl^- RDF, the figure in the middle shows the Na^+ - Na^+ RDF and the lower figure shows the Cl^- - Cl^- RDF.

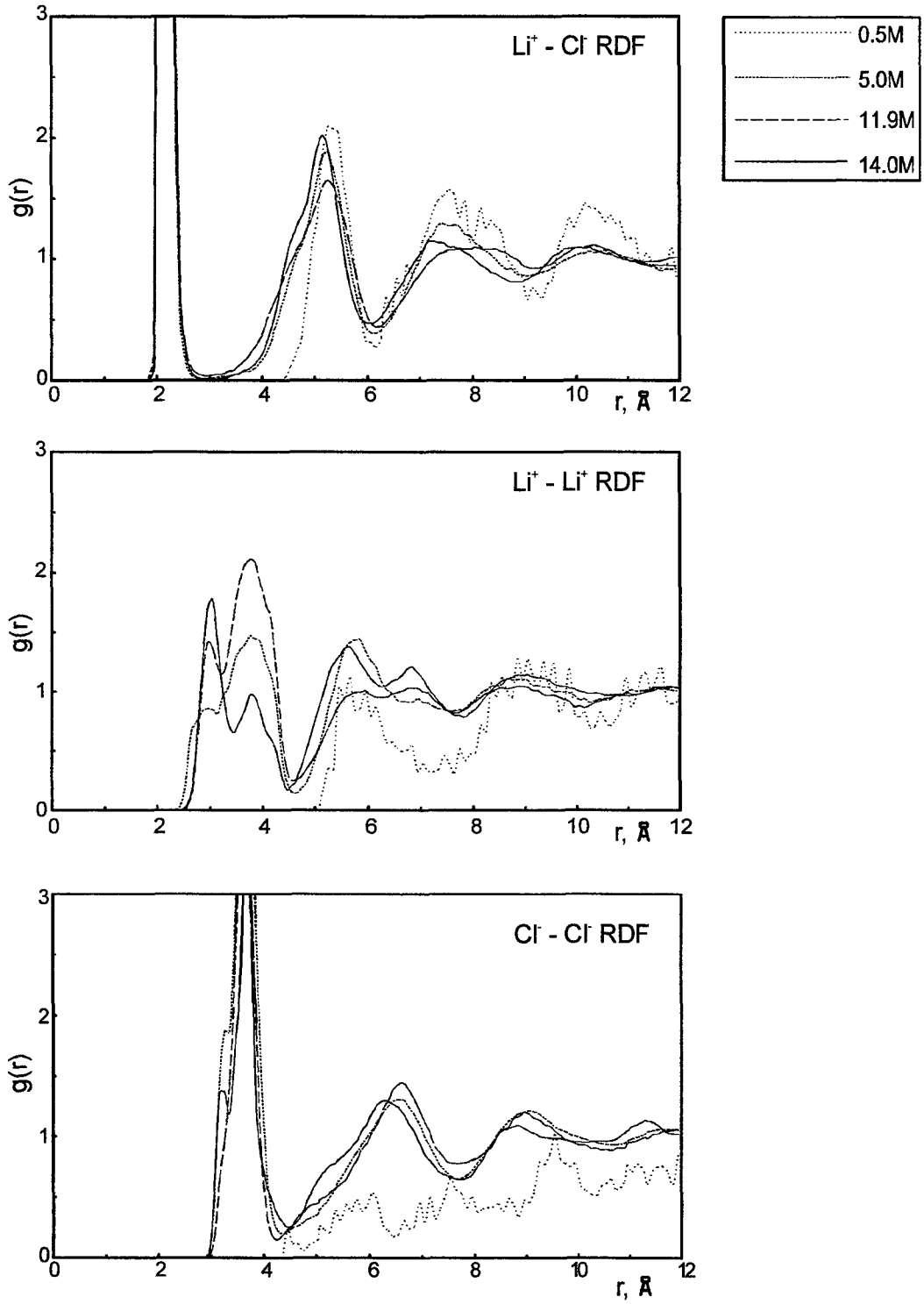

Fig. 4. The ion – ion radial distribution functions for LiCl solutions with concentrations: 0.5 M, 5.0 M, 11.9 M and 14.0 M. The upper figure shows the Li^+ - Cl^- RDF, the figure in the middle shows the Li^+ - Li^+ RDF and the lower figure shows the Cl^- - Cl^- RDF.

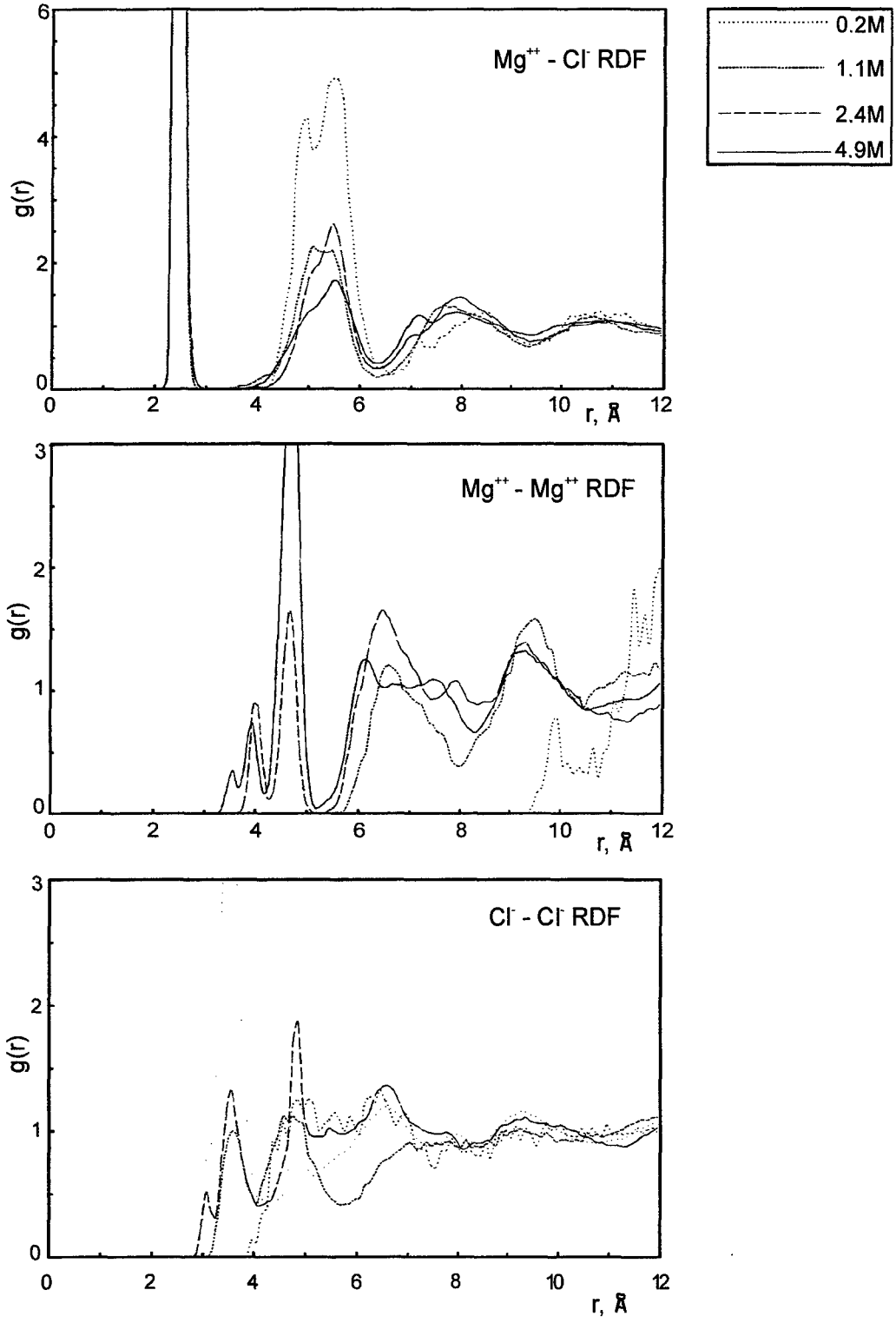

Fig. 5. The ion – ion radial distribution functions for $MgCl_2$ solutions with concentrations: 0.2 M, 1.1 M, 2.4 M and 4.9 M. The upper figure shows the Mg^{2+} - Cl^- RDF, the figure in the middle shows the Mg^{2+} - Mg^{2+} RDF and the lower figure shows the Cl^- - Cl^- RDF.

The pair distribution function gives only a spherically averaged information about the system structure and the nonspherical ionic associations are sometimes masked. However, in the case of the concentrated NaOH, NaCl and LiCl solutions the presence of the ionic aggregates can be easily observed. We describe the correlations exhibited in Figure 2 (the NaOH case) in a more detailed way.

The cation – cation RDF (Fig. 2, middle part) significantly changes with the increase of the NaOH concentration. In the solution with the lowest concentration the positions of sodium ions are not correlated. In the case of 3 M solution there are three peaks visible at 3.2, 6.0 and 9.0 Å. The first peak corresopnds to two Na^+ ions separated by a H_2O molecule. The position of the first maximum moves to 3.1, 3.0, 2.95 and 2.9 Å in 6 M, 10 M, 14 M and 19 M solutions, respectively. Beginning from the 6M NaOH solution, the cation – cation RDF's exhibit peak typical to the crystal-like arrangement at 4.2 Å, corresponding to two sodium ions separated by two hydroxyl ions. Similar tendency could be observed for the anion – anion RDF plots. There are no correlations in 0.5 M solution, in 3 M (and more concentrated) solutions the maxima at 3.1, 6.3 and 8.9 Å are appearing as the number separated and Na^+ separated ion pairs increases. The cation – anion pair distribution functions show three peaks at 2.1 Å, about 5 Å and 7.6 Å. The position of the second peak changes from 5.2 to 4.7 Åwith the increase of the concentration. These data suggest that with the increase of the concentration the hydrated ions probably merge into ion-pair solvated complexes. Further increase of the concentration leads to appearance of multi-ionic structures and, finally, solvated crystals. The plots of the RDFs undoubtely suggest the presence of higher ionic aggregates in concentrated NaOH solutions and, for the highest concentrations, the appearance of hydrated lattice-like structures.

Similar conclusions result from the analysis of the ion – ion radial distribution functions for NaCl and LiCl solutions (Figures 3 and 4, respectively).

Figure 5 represents somewhat different case: magnesium chloride, which is non-symmetric solution. All the RDF's change significantly with the increase of the $MgCl_2$ concentration. Let us begin with the Mg^{2+} - Mg^{2+} correlations. In the solution with the lowest concentration, 0.2 M, the positions of magnesium ions are not correlated. In the case of 1.1 M solution we observe two peaks at relatively large distances, 6.8 Å and 9.3 Å. From the concentration 2.4 M $MgCl_2$ upwards, the cation – cation RDFs exhibit peaks typical to the crystal-like arrangement at 4.0 Å and 4.8 Å, corresponding to two Mg^{2+} ions in contact through the Cl^- bridge and H_2O bridge, respectively. Similar tendency is observed for the Cl^- - Cl^- RDF. We do not observe any anion – anion correlations in 0.2 M solution. From the concentration 1.1 M upwards, the RDFs exhibit the maxima at 3.8 Å, 4.9 Å which correspond to the solvent separated and Mg^{2+} separated anion pairs. The cation – anion RDFs show three peaks at 2.3 Å, around 5.3 Å and 7.2 Å but the peak at the lowest distance does not appear in the 1.1 M solution. The structure of the Mg^{2+} - Cl^- RDF at the highest concentrations resembles typical RDFs for crystalline media. The evolution of the RDFs with the increase of the $MgCl_2$ concentration clearly reflects the process of merging of the solvated ions into solvated ion-pair complexes and further into multi-ion structures.

3.2. Voronoi polyhedra

Studies of the radial distribution functions have been completed by the calculations of the Voronoi polyhedra for the cation – anion coordination in the NaOH and $MgCl_2$ solutions. For a given cation (Na^+ or Mg^{2+}) we bulid the Voronoi polyhedron taking into account all the anions in the system. The calculation is repeated for all the cations in the simulation box and then repeated for a large number of the ion configurations in the simulation box recorded in the course of the simulation. The system of the polyhedra was then analysed with the aim to estimate a degree of order in the ionic structures. From many possible versions of such analysis (*e.g.* plotting the distributions of the number of walls of the polyhedra, calculating the effective coordination numbers, *etc.*) we include in the present paper the distributions of the anisotropy factor of the polyhedra and their evolution with the increase of the ion concentration.

Figure 6 shows the α-parameter distributions for the NaOH solutions with the concentrations 0.5 M, 10 M and 19 M (upper part of the figure) and for the $MgCl_2$ solutions with the concentrations 0.2 M, 2.4 M and 4.9 M (lower part). The distribution for the random system of the Lennard – Jones particles is given also in the figures. For very low concentrations (not shown in the figures) the α distributions resemble the distributions for the random system. Then, with the increase of the concentration the simulated distributions steadly evolve towards the distributions for the distorted fcc or bcc lattices. Figure 6 provides thus an additional support for the presence of multi-ion ordered structures in concentrated solutions.

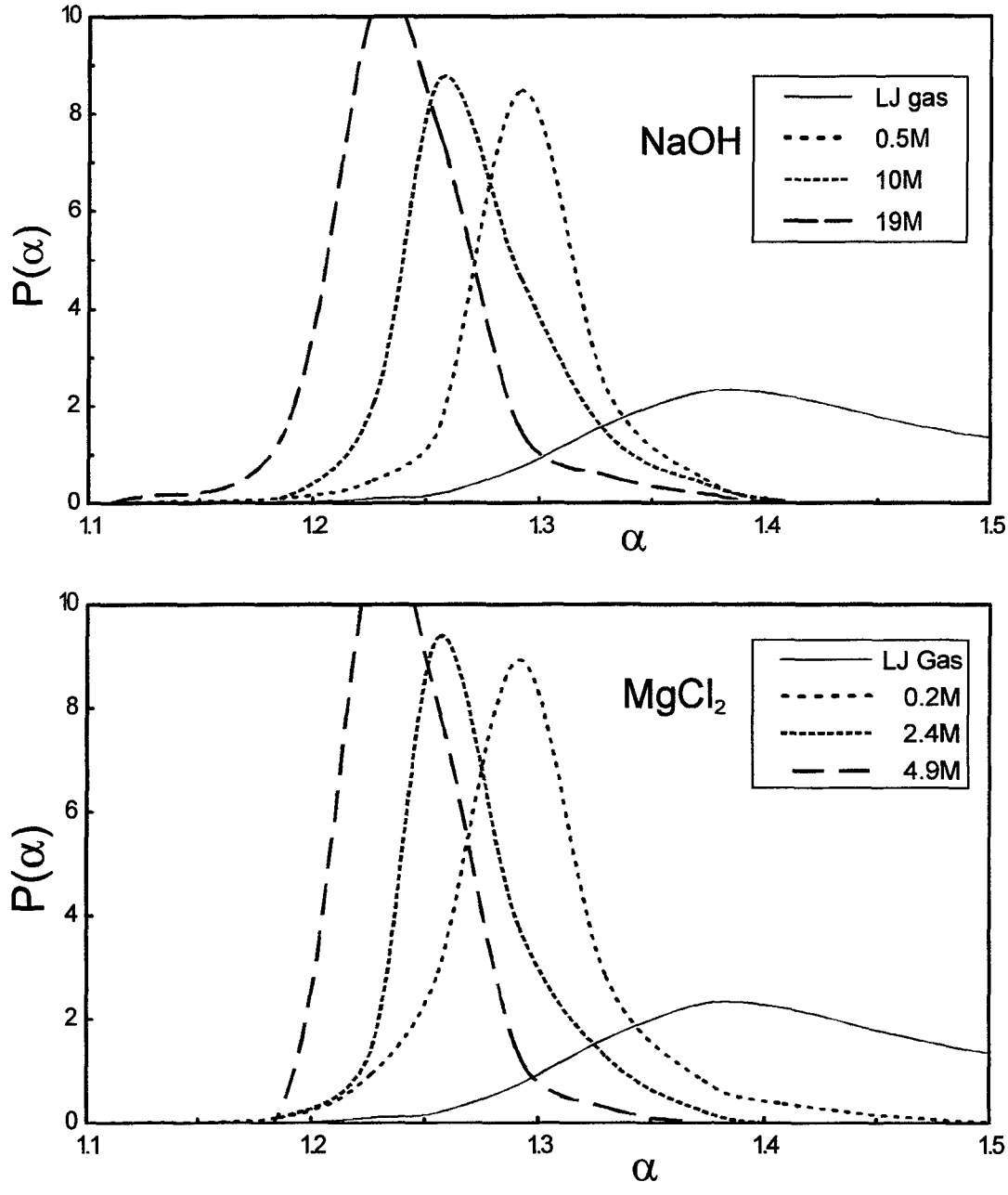

Fig. 6. Distributions of the anisotropy parameter α for the NaOH solutions with the concentrations 0.5 M, 10 M and 19 M (upper part of the figure) and for the $MgCl_2$ solutions with the concentrations 0.2 M, 2.4 M and 4.9 M (lower part). The distribution for the random system of the Lennard – Jones particles is given also in the figures.

4. CONCLUSIONS

The results of the simulations of the concentrated ionic solutions allow us to formulate the following conclusion. For a wide range of of concentrations, from 1 M to 20 M, the geometry of the ionic configurations is significantly different from the geometry of a random set of points.

This conclusion is based on the analysis of the ion – ion radial distribution functions and on the comparison of the characteristics (such as distribution of the anisotropy coefficent or the distribution of the number of faces) of the Voronoi polyhedra constructed around the ions in the simulation box to the distribution calculated for the random tesselation of space. The Voronoi polyhedra for the simulated ion configurations in solutions have similar characteristics as the polyhedra drawn for the slightly distorted regular lattices of ions.

On a basis of these results, we can put forward a conjecture that regions or domains of the quasi-crystalline order of ions exist in the concentrated solutions. The quasi-crystalline order is more evident for lower part of the concentration range, between 1 M and 5-6 M. For the highest concentrations, the structure of the ionic configurations was determined not only by the ion - ion interactions but, perhaps even predominantly, by the interactions between the ions and the solvent molecules which belong at the same time to more than one solvation sphere. Finally, the increase of the charge of the cation, like Mg^{2+}, results in a more pronounced quasi-crystalline order. It seems that the results of the simulations of the concentrated ionic solutions support to a large extent the lattice theory of concentrated electrolytes.

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