

Structural and dynamical properties of concentrated aqueous NaOH solutions: a computer simulation study[☆]

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Received 30 July 1999; received in revised form 8 October 1999; accepted 8 October 1999

Abstract

Molecular dynamics simulations of NaOH aqueous solutions have been performed with a flexible model of the water molecule. Ion–ion interactions have been described by the (12–6) Lennard–Jones type and coulomb potentials. The concentration of the solutions ranged from 0.5 to 19 M. The structures of hydration shells of the ions were analysed using the radial distribution functions, Voronoi tessellations, the running and O’Keeffe coordination numbers and other tools. Structural properties obtained from simulations agreed reasonably well with results of the available experimental data. The dynamical properties were calculated and compared with experimental measurements. A particularly careful analysis was applied to the topological properties of the ionic structures in solution. The results of calculations suggest an existence of the ordered structures of ions in solution and supports the Ruff theory of ionic quasi-lattices in concentrated solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sodium hydroxide; Molecular dynamics; Pseudo-lattice theory; Concentrated ionic solutions; Voronoi polyhedra

1. Introduction

Structure of ionic solutions is of great importance in many areas ranging from radiation chemistry to biology. A large number of papers have been published concerning ionic hydration phenomena, especially for low and moderate concentrations of alkali halides (see Burgess, 1978; Marcus, 1986 for references). Shortly after the first successful simulation of pure water by Stillinger and Rahman (1974) various computer simulations of the ionic solutions have been reported (Heinzinger and Vogel, 1974; Pálinkás et al., 1977).

With a few exceptions (Payne et al., 1994; Tamura et al., 1988), most of the calculations concerned the solvation structures of ions. The ion–ion correlations were neglected or, at best, investigated by use of the radial distribution functions only. We focus our interest on the properties of the concentrated aqueous solutions of sodium hydroxide and inter-ionic associations in those solutions.

The aqueous solutions of electrolytes represent a complicated case and cannot be described by an analytical theory in the full range of concentrations. For low concentrations of ions, there are theoretical models that work reasonably well. The Debye–Hückel or the mean spherical theory can be given as the examples (see Gurney, 1963 for references). At the high concentration range, the validity of the models deteriorates very quickly and different theory should be applied. The idea of lattice-like model of solutions (Ghosh, 1918) preceded even the Debye–Hückel theory. Frank and

[☆] Workshop on New Trends in Computational Methods for Large Molecular Systems, Szklarska Poreba, Poland, 1–6 July 1999, Edited by W. Andrzej Sokalski and Morris Krauss.

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Thompson (1959) have provided the consequent formulation of the lattice theory of electrolytes. Bahe (1972) introduced the diffuse lattice-like model, assuming dielectric gradient region around each ion.

In a series of papers Ruff and co-workers gave the most complete theory of the concentrated electrolytes (Ruff, 1977; Ruff et al., 1981). Their model can be described as follows: (1) the ions are distributed in a lattice-like arrangement. The positions of the ions deviate randomly from the lattice sites; (2) the ions are immersed in continuous dielectric; (3) the dielectric gradient region in the vicinity of ions causes repulsive force between ions.

In modern investigations the computer simulations play an important role, occupying the place between the theory and experiment. In some cases the computer experiment can be used to check some aspects of ana-

lytical theories. The aim of the present work is to perform such a verification of the Ruff theory by comparing the most important of its predictions, i.e. the lattice-like arrangement of the ions, with the results of the computer experiment.

2. Method of calculations

2.1. Simulation details

The simulations have been performed by the molecular dynamics method (Allen and Tildesley, 1994). The simulation box was assumed in a cubic form with the size ranging between 25 and 35 Å, depending on the concentration. The following concentrations of the NaOH solutions were investigated: 0.5, 3, 6, 10, 14 and

Table 1
Interaction parameters^a

Molecule	Centre	Valence		Non-bond		
		Bond (Å)	Angle (°)	Distance (Å)	Energy (kcal/mol)	Charge
H ₂ O	H	0.354	180.00	2.886	0.044	0.417
H ₂ O	O	0.658	104.51	3.500	0.060	−0.834
OH [−]	H	—	—	2.886	0.044	0.182
OH [−]	O	—	—	3.500	0.060	−1.182
Na ⁺	Na	—	—	2.983	0.030	1.000

^a The homonuclear valence parameters, homonuclear Lennard–Jones parameters and charges of each interacting centre. Heteronuclear parameters were obtained through the use of combination rules.

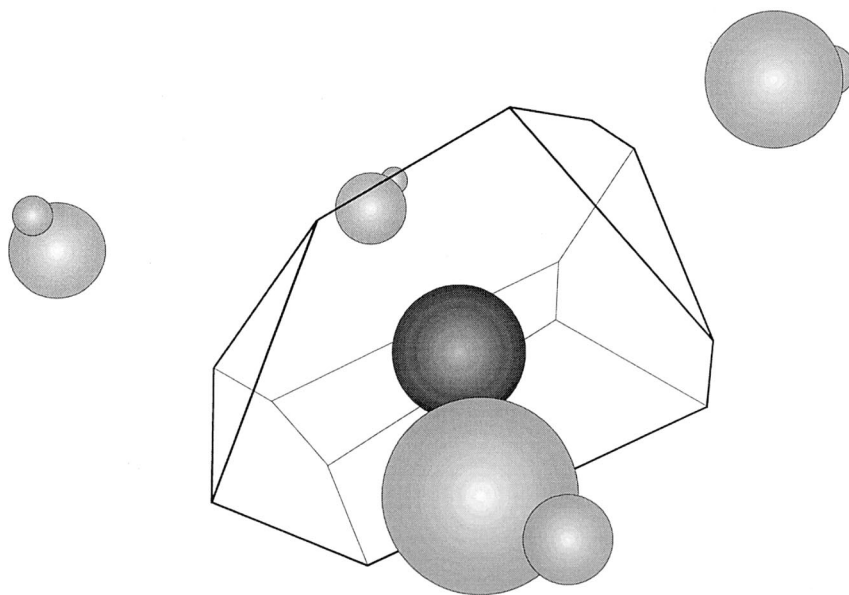


Fig. 1. Voronoi polyhedron constructed for the Na⁺ ion surrounded by OH[−] anions. A snapshot from the simulation of 14 M NaOH.

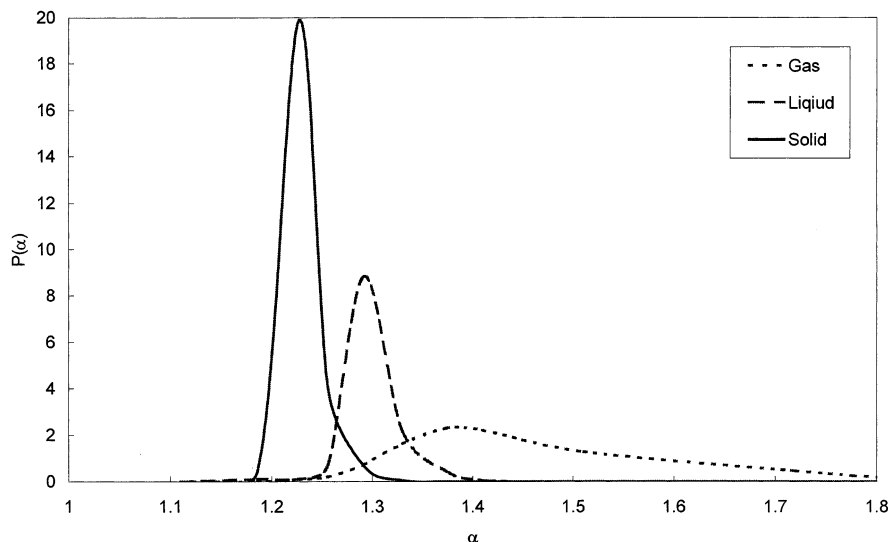


Fig. 2. Distributions of the anisotropy parameter α for model systems of the Lennard–Jones particles.

19 M. The box typically contained about 400 water molecules and the number of ions that resulted from the concentration of the solution. 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 (Rappé et al., 1992) and the shifted force method for non-coulombic interactions has been applied. The flexible model of the water molecule has been used. The Lennard–Jones parameters, the charges and details of the model of water are given in Table 1. The periodic boundary conditions have been employed with the Ewald summation (Ewald, 1921) for calculations of the long-range electrostatic forces. A typical simulation run was composed of three stages: (a) the initial, equilibration phase with the temperature scaling of $1/2 \times 10^4$ time steps, (b) the control phase of 1×10^4 time steps and (c) the proper simulation of $4/8.5 \times 10^4$ 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 and stochastic Voronoi polyhedra.

2.2. Voronoi polyhedra analysis

The most widely used quantity in structural studies is the radial distribution function. Unfortunately, this function gives only spherically averaged information about the system structure. Therefore, another method should be introduced to describe spatial correlations in solution.

Voronoi polyhedra (Okabe et al., 1992) seem to be a very convenient tool for an examination of the local

multi-particle structure in condensed phases. Voronoi diagram is a convex region of space closer to the central particle than to any of the medium atoms of the system. The Voronoi diagrams in 3D space (Fig. 1) can be considered as a generalisation of the Wigner–Seitz symmetric cells. The first Voronoi polyhedra analysis was performed by Bernal for the random packing system (Bernal, 1964). It was applied to study the structure of liquid water (Shih et al., 1994), the traps for an excess electron (Bartczak et al., 1989) and aqueous solutions of aminoacides (David and David, 1983) or electrolytes (Zapalowski and Bartczak, 1997). Various methods of analysis were used: the volume distribution (Gil Montoro and Abascal, 1993), the number of faces distribution (Cape et al., 1981), signature of the polyhedra (Tanemura and Hiwarati, 1977). It was also demonstrated (Gil Montoro et al., 1994) that analysis of the non-sphericity (or anisotropy) factor of the Voronoi polyhedra is suitable for the study of the structure of disordered systems. Non-sphericity parameter is given by:

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

where A and V are surface and volume of the Voronoi polyhedron. For a sphere α equals to 1, for the bcc, fcc and simple cubic lattices it equals 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 (Fig. 2). For less-ordered systems the distribution is much broader and exhibits a bell-shaped form: for liquid water α ranges from 1.3 to 2.0 with maximum at 1.65 (Ruocco et al., 1991).

Several authors proposed unambiguous definitions of the coordination numbers. One of the first attempts was based on the number of faces of the Voronoi polyhedron (Frank and Kasper, 1958). Unfortunately it worked correctly only in case of nearly ordered systems. All the Voronoi cells in an ideal crystal are identical and the number of faces is consistent with the coordination number. When the ion positions deviate from the lattice sites, we observe rapidly increasing variety of the shapes of the Voronoi polyhedra. Each face of the Voronoi polyhedron corresponds to the nearest neigh-

bouring atom in a given direction, but the faces corresponding to the distant atoms are very small and only the large faces are connected with the real neighbours. According to the definition of the coordination number Z^* proposed by O'Keeffe (1979), the contribution of a given medium atom to the coordination number is weighted by the solid angle of the corresponding face of the Voronoi polyhedron. While the number of faces of the polyhedron is usually too high, the O'Keeffe coordination numbers are from the same range as the experimentally determined ones.

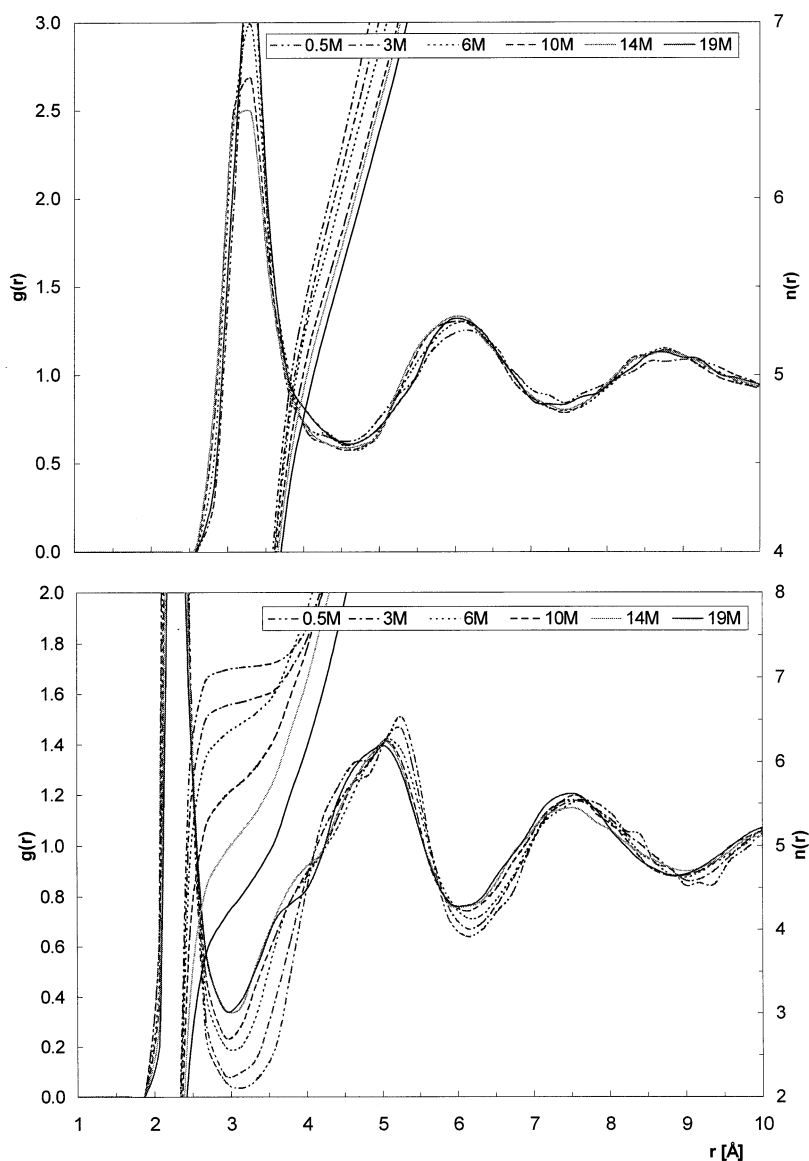


Fig. 3. Ion–water (oxygen) radial distribution functions and running integration numbers. The upper part: OH^- –water, lower part: Na^+ –water RDFs. The NaOH concentrations are marked in the figures.

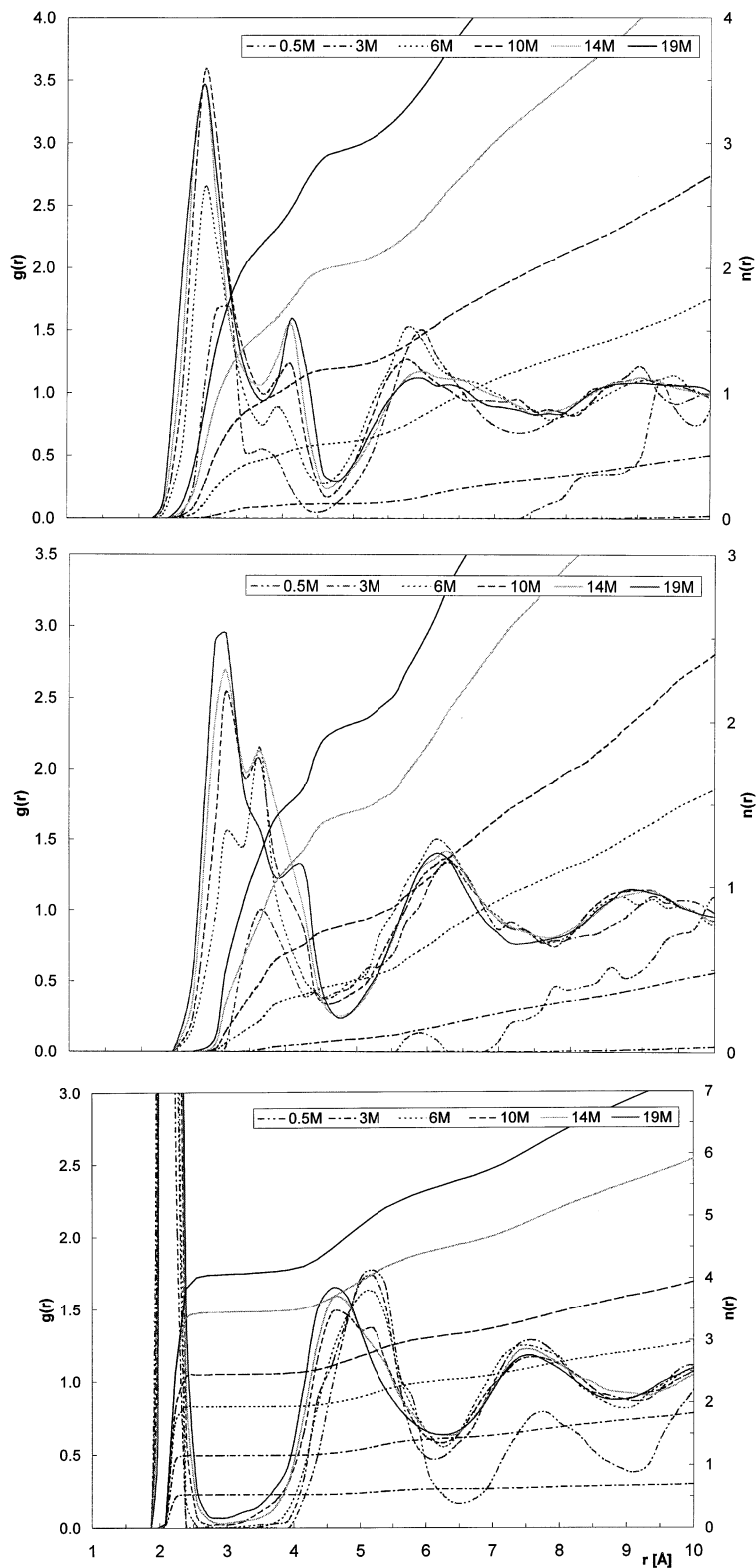


Fig. 4. Ion–ion radial distribution functions and running integration numbers: Na⁺–Na⁺ (the upper figure), OH[–]–OH[–] (the middle figure) and Na⁺–OH[–] (the lower figure). The NaOH concentrations are marked in the figures.

3. Results and discussion

3.1. Radial distribution functions

The ion–water (oxygen) and ion–ion pair distribution functions are plotted in Figs. 3 and 4. The structure of bulk water seems to be significantly modified comparing to that of pure water even for the lowest concentration of the NaOH solution. However, further increase of the NaOH concentration does not cause the significant changes in the water–water RDFs. The calculated $\text{Na}^+\text{--H}_2\text{O}$ bond length is 2.4 Å and agrees with the experimental diffraction data (Ohtomo and Arakawa, 1980). With the increase of the NaOH concentration the first hydration shell becomes less pronounced. The plateau of the RDFs at the distance of 3.0 Å disappears and the edge of the first hydration sphere becomes poorly defined. The running coordination number ranges from 7.1 (0.55 M solution) to 4.2 (19 M). The experimental hydration number of Na^+ is distributed over the range from 4 to 7 depending on the measurement method (Ryss and Radchenko, 1964; Soper et al., 1977; Pálinkás et al., 1980; Othaki and Radnai, 1993). The second hydration shell with the centre at the distance of 5.1 Å for lower concentrations and 4.9 Å for higher ones is well established.

The OH^- ion is known as a structure-making anion. Because of relatively small effective ionic radius (1.33 Å) and presence of unbonded electrons it promotes the creation of hydrogen bonds. The hydration structure of the OH^- ion is rather strong and remains almost unchanged with the increase of the NaOH concentration. The structure of the OH^- hydration shell in diluted solutions is very similar to the crystal structures

of the NaOH hydrates (Mootz et al., 1994). The observed ion–water bond length is 3.0 Å and the running coordination number ranges from 5.5 to 6.3 and is independent of the concentration of the solution. The experimental hydration numbers are from the range 3/6 (Brady and Krause, 1957; Kunze et al., 1985). The second hydration shell is also clearly visible, the distance between the ion and the centre of the shell is 6.2 Å. A much lower third peak appeared at the distance of 8.8 Å.

The pair distribution function gives only an averaged information about the system structure and the associations are often masked. However, in the case of the concentrated NaOH solutions the presence of the ionic aggregates can be easily observed. The cation–cation radial distribution function significantly changes with the increase of the NaOH concentration. In the diluted solution the positions of the 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 corresponds 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, 10, 14 and 19 M solutions, respectively. Beginning from the 6 M NaOH solution, the cation–cation RDFs exhibit peak typical to the crystal-like arrangement at 4.2 Å, corresponding to two sodium ions in contact with one hydroxyl ion. Similar tendencies could be observed for the anion–anion RDF plots. There are no correlations in the 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 of the solvent and Na^+ separated ionic pairs increases. The cation–anion pair distribution functions show three peaks at 2.1, about 5 and 7.6 Å. The position of the

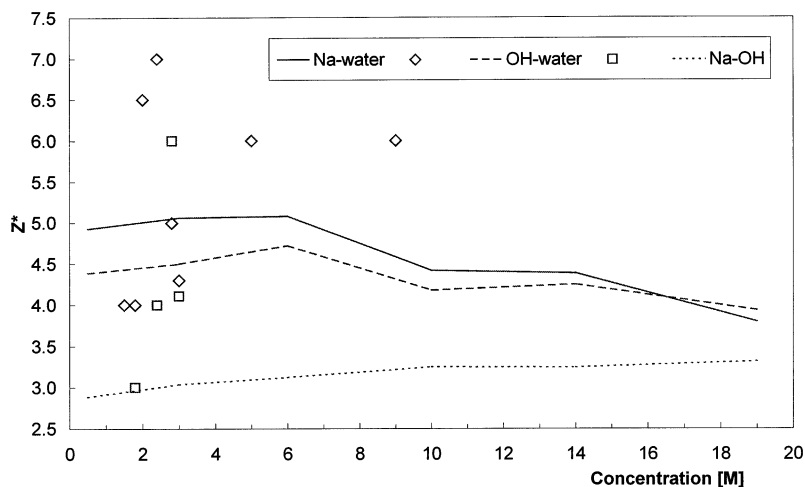


Fig. 5. O'Keeffe coordination number as a function of the concentration. The water coordination around Na^+ (full line, diamonds) and OH^- (broken line, squares) and OH^- coordination around Na^+ ions are shown in the figure. Different experimental values are marked in the figure as diamonds and squares (see the text for references).

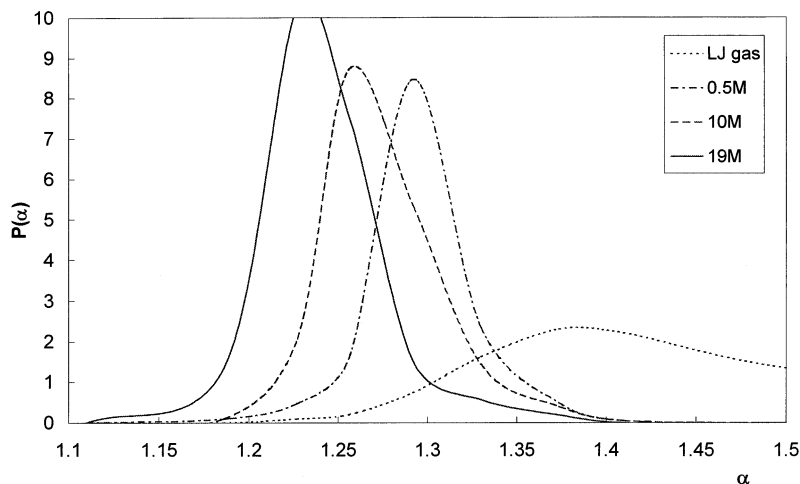


Fig. 6. Distributions of the anisotropy parameter α for 0.5 M NaOH, 10 M NaOH and 19 M NaOH solutions. The dotted curve shows the distribution for the Lennard–Jones gas.

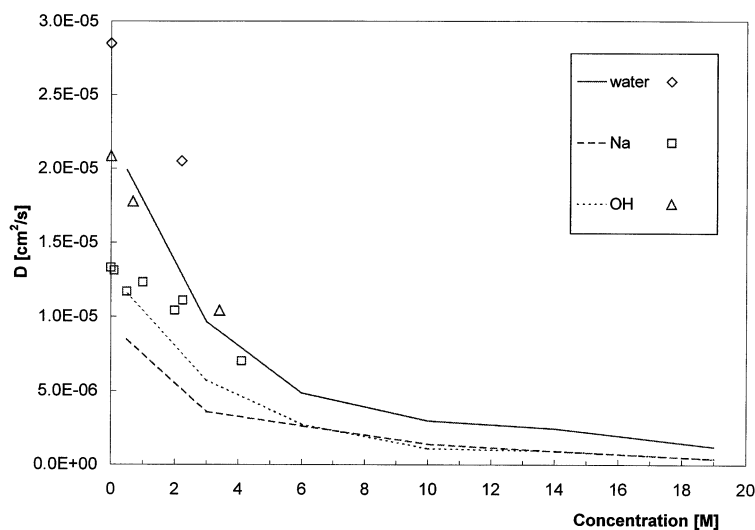


Fig. 7. Self-diffusion coefficients of H_2O , Na^+ and OH^- ions as a functions of the NaOH concentration. The experimental values for H_2O , Na^+ and OH^- coefficients are marked by diamonds, squares and triangles, respectively (see the text for references).

second peak changes from 5.2 to 4.7 Å with the increase of the concentration. On a basis of the experimental data some authors (Dorosh, 1976) suggest that with the increase of the concentration the solvated ions could merge into ion-pair solvated complexes. Further increase of concentration causes the appearance of multinuclear ionic structures and, finally, solvated crystals. The radial distribution functions undoubtedly suggest the presence of higher ionic aggregates in concentrated NaOH solutions. The shifts of some peaks towards the shorter distances as observed for 6 M and more concentrated solutions could be interpreted as an

effect of the appearance of hydrated lattice-like structures.

3.2. Voronoi analysis

Fig. 5 shows the O’Keeffe Z^* coordination number as a function of the concentration. The plots describe the coordination of anions around a cation and the hydration of cations and anions. The O’Keeffe hydration numbers of Na^+ depend on the concentration and are ranging from 3.9 (high concentrations) to 5.1 (low concentrations). The hydration numbers of OH^- ion are also decreasing with the increase of the concentra-

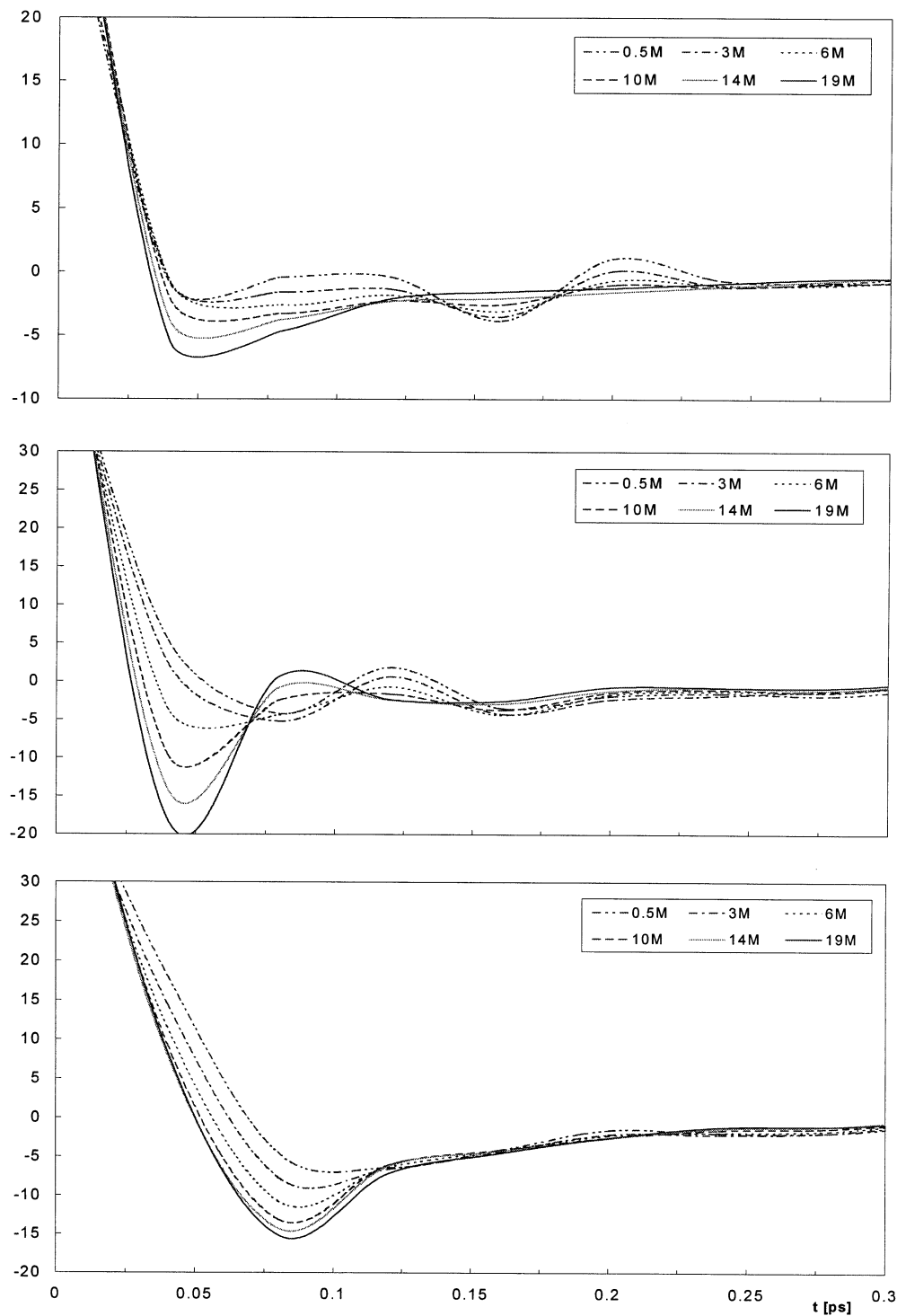


Fig. 8. Velocity autocorrelation functions for Na^+ (the upper figure), OH^- (the middle figure) and H_2O molecules (the lower figure) calculated for a series of NaOH solutions with concentrations: 0.5, 3, 6, 10, 14 and 19 M.

tion and are from the range from 4.0 (19 M solution) to 4.7 (6 M). The decrease of the hydration number is probably caused by deficiency of water molecules in more concentrated solutions. The $\text{Na}^+\text{--OH}^-$ coordination number appears to be rather independent of concentration. It increases slightly from 2.8 in 0.55 M to 3.1 in the highest concentrations. The Z^* numbers are generally smaller than the coordination numbers obtained by integrating of the pair distribution functions, but they fit well to the experimental values. We must emphasise that Z^* does not depend directly on the distance between centres opposite to the running integration number, that means it informs us how many neighbours are around the investigated centre, but not how distant they are. Because of such feature of Z^* its changes with the increase of the concentration are relatively smaller comparing to that of corresponding running integration number.

Fig. 6 shows the α parameter distributions for investigated solutions. The non-sphericity distributions of the $\text{Na}^+\text{--OH}^-$ polyhedra at low concentrations exhibit peaks close to that of the Lennard–Jones liquid (Fig. 2). For increasing concentration the distribution of the Voronoi polyhedra resembles the distribution for the solid. This strongly suggests a form of quasi-crystalline structure of ions in concentrated NaOH solutions.

3.3. Dynamical properties

Fig. 7 presents the self-diffusion coefficients both calculated from the mean squared displacement and obtained experimentally (Hertz, 1973; Nikiforov, 1975; Tyrrell and Harris, 1984), as a function of the concentration. The diffusion coefficients of all the species present in solution decrease rapidly with the increase of the concentration. The mobility of water molecules remains somewhat higher than ionic in a full range of concentrations. In the diluted solutions the OH^- ions move faster than the Na^+ ions. From 6 M NaOH solution the diffusion coefficients of the both ions are almost the same. It is clearly visible that the ions exist as the two- or multi-ionic aggregates and the process of aggregation begins for 3 M and more concentrated solutions.

The velocity autocorrelation functions for Na^+ , OH^- and H_2O are shown in Fig. 8. The functions change shape with the increase of the concentration. We observe a noticeable increase in the first minima, especially in the case of OH^- . At high concentrations rebounding collisions are more numerous, which causes the function to deepen the first minimum. The most significant changes could be observed for 14 and 19 M solutions. This suggests the increase of the caging effects with the increase of the concentration: for the

most concentrated solutions the hydration cage is replaced by firm ionic crystal-like structure.

4. Conclusion

The results of the simulations of the NaOH solutions allow us to formulate the following conclusions. For a wide range of concentrations, from 6 to 19 M, the postulated (Chizhik et al., 1986) presence of the multi-ion structures has been established. The radial distribution functions as well as the distributions of the non-sphericity factor of the Voronoi polyhedra strongly suggest the existence of the crystalline-order regions in 14 and 19 M NaOH solutions.

The results of the simulations support the lattice theory of concentrated electrolytes. However, the analysis based on the Voronoi tessellations has a qualitative character and we need more powerful tools to describe lattice structures more quantitatively. This work is currently in progress in our laboratory.

Acknowledgements

This work has been supported by the Polish Government as the KBN Project 3 T09A 066 17.

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