An Investigation of the Structure of Aqueous Electrolyte Solutions by Statistical Geometry

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Statistical geometry is employed for a quantitative description of deviations from regular octahedrality of water around monovalent ions and from regular tetrahedrality of solvent water around water molecules. For these deviations a new criterion is presented by taking into account octahedral and tetrahedral spatial symmetry groups. A geometrical definition of structure making and structure breaking is proposed and illustrated on the basis of molecular dynamics simulations of 2.2 molal aqueous KCl and LiI solutions with the flexible BJH model of water.

1. Introduction

The description of liquid structures by methods of statistical geometry is a long-standing problem in the theory of the liquid state. Bernal [1] was the first who suggested to use Voronoi polyhedra (VP). Recently, Ruocco et al. [2] introduced an asphericity parameter for the description of deviations from spherical symmetry. Their main aim was the investigation of the self-diffusion process of water based on the approach by Cohen and Turnbull [3], which takes into account both the volume and the shape of the "cage" surrounding the central molecule [4]. Another way to describe liquid structures by statistical geometrry is a network of tetrahedra and octahedra which are called Delauney simplices (DS) [5]. A generalization of DS's for molecular liquids has been reported recently [6]. With such an approach the deviation from an ideal structure of a molecular liquid can be described. The vital role of geometrical peculiarities for the description of the structure of water and aqueous solutions has been noted in a series of investigations [7–9]. It remains an important problem to describe quantitatively structure deviations in solutions which are normally called structure making or structure breaking [10, 11]. In this paper we try to give a quantitative measure of structure breaking around ions and hydrophobic species, which is based on the statistical geometry approach.

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2. Measures of Deviation from Regular Octahedrality and Tetrahedrality

Medvedev and Naberukhin [5] were the first who introduced quantitative measures for the deviations from regular tetrahedrality and octahedrality. They defined the quantities

$$T' = \sum_{i>j}^{15} (l_i - l_j)^2/(15\bar{l}^2) \tag{1}$$

and

$$Q' = \left(\sum_{\substack{i>j \\ i,j\neq m}}^{15} (l_i - l_j)^2 + \sum_{i\neq m}^{5} (2^{1/2}\cdot l_i - l_m)^2 \right) \Big/ 10\bar{l}^2 \tag{2}$$

for the deviation from regularity of a tetrahedron and a quartoctahedron, respectively, where l_i is the length of the i-th edge of the simplex, $\bar{l}$ the average length (l_m excluded), and l_m the longest distance between two vertices of the octahedron, l_m being common to the four quartoctahedra into which the octahedron is divided. The average of the four Q' values is defined as the deviation O' from regularity of the octahedron.

It is generally accepted that the four nearest neighbour water molecules around a central one tend to arrange tetrahedrally. Also, for monovalent cations the six nearest water molecules prefer an octahedral symmetry, as is known from experiments as well as theoretical considerations [10]. The position of the water molecules is taken to be that of their oxygen atoms.

We distinguish three kinds of water: octahedral water, hydration water, and bulk water. Octahedral water consists of the six nearest water molecules neighbouring the ions. Hydration water is defined in

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the conventional way by the integral up to the first minimum of the ion-oxygen RDF; the hydration number N_H may differ from six. The sum of hydration and bulk water we call total water.

The deviation from regular octahedrality of octahedral water is given by $O = \langle O' \rangle$, where the average is taken over all ions of the same kind. The deviation from regular tetrahedrality of bulk water (T_{bulk}) and hydration water (T_{hydr}) is defined by averaging, $T = \langle T' \rangle$, over all bulk water molecules and all hydration water molecules of all ions of the same kind, respectively. The position of the ion is taken to be the position of one of the four nearerst water molecules surrounding a hydration water molecule.

A check of O and T shows that for real solutions these measures differ only little for different ions and do not reflect significantly peculiarities of ionic hydration. Therefore we suggest here additional measures. Again we use primed and unprimed symbols for individual and averaged values, respectively. For deviations from octahedral symmetry we consider vectors $\boldsymbol{I}_1, \boldsymbol{I}_2, \boldsymbol{I}_3$, which are the sum of the vectors directed from one vertex towards its four nearest vertices plus the sum of the vectors directed from the opposite vertex towards its four nearest vertices:

$$\begin{aligned} \boldsymbol{I}_1 &= \sum_{\substack{j=A \\ j \neq D,B}}^{F} (\boldsymbol{r}_{Dj} + \boldsymbol{r}_{Bj}), \\ \boldsymbol{I}_2 &= \sum_{\substack{j=A \\ j \neq F,A}}^{F} (\boldsymbol{r}_{Aj} + \boldsymbol{r}_{Fj}), \\ \boldsymbol{I}_3 &= \sum_{\substack{j=A \\ j \neq C,E}}^{F} (\boldsymbol{r}_{Cj} + \boldsymbol{r}_{Ej}), \end{aligned} \tag{3}$$

where A, B, C, D, E and F stand for the vertices of the octahedron. The scalar invariant of this group can be written as

$$I' = \boldsymbol{I}_1^2 + \boldsymbol{I}_2^2 + \boldsymbol{I}_3^2 . \tag{4}$$

Different from the insensitivity of O for differences between ions, $I = \langle I' \rangle$ is invariant for symmetric dilatations, for which O is sensitive. Thus, the criterion of deviation from regular octahedrality is best expressed by the sum of both:

$$O_v = I + O . \tag{5}$$

Analogously, for tetrahedrality one may consider the sum of the vectors $\boldsymbol{r}_{iw}$ directed from the position of the central water molecule of the tetrahedron to the i-th vertex:

$$\boldsymbol{T}' = \frac{1}{4\bar{r}} \left(\sum_{i=1}^{4} \boldsymbol{r}_{iw} \right), \tag{6}$$

where $\bar{r}$ is the average distance between the central water molecule and the four vertices. It is straightforward to write down a scalar invariant as a measure of the deviations from regular tetrahedrality:

$$\theta = |\boldsymbol{T}| + T \quad \text{where} \quad |\boldsymbol{T}| = \langle |\boldsymbol{T}'| \rangle . \tag{7}$$

Deviations from Delauney simplices could also be defined by the deviations of the simplex angles from the ideal ones. But it is the main advantage of the approach proposed here that O_v and θ can be calculated much more easily from the simulation. In addition, the angular criterion proved to be insensitive when employed for the calculation of the deviation of water structure around hydrophobic and hydrophilic solutes [6].

3. Details of the Simulations

Molecular dynamics simulations of 2.2 molal LiI and KCl solutions (200 water molecules and 8 ion pairs per periodic cube) were performed. The water-water interactions were described by a modified central force potential (BJH model) which has proved its usefulness in simulations of various aqueous systems [12]. The ion-water and ion-ion potentials for the LiI solution were taken from [13]. While the potassium-water potentials were derived from ab-initio calculations [14], the chloride-water and ion-ion potentials for the KCl simulation were taken from [15]. For more detailed informations the reader is referred to the original publications cited. The shifted force method was employed for the short range interactions while the Ewald method was used to calculate the Coulomb interactions. The timestep was $2.5 \cdot 10^{-4}$ ps. The simulations were extended over 7.5 ps and 5.0 ps for the LiI and KCl solutions at an average temperature of 310 K and 299 K, and with sidelengths of the periodic cubes of 18.68 Å and 18.74 Å, respectively.

4. Static Properties

The O_v values of the octahedral water of Li^+, K^+, Cl^- and I^- in the 2.2 molal aqueous solutions of LiI

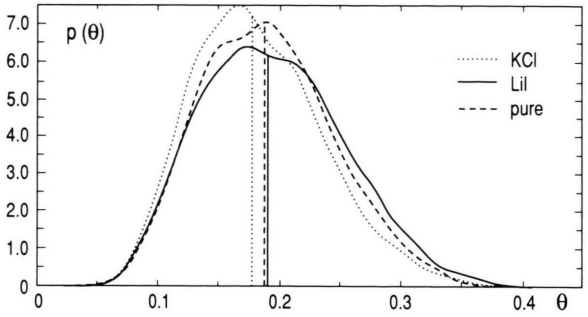

Fig. 1. Normalized distributions of θ for pure water and bulk water in the 2.2 molal KCl and LiI solutions. The average values are marked on the abscissa.

Table 1. Hydration number N_H and average deviation O_v from regular octahedrality and from regular tetrahedrality θ with an uncertainty of ± 0.02. AVDIST are average distances between water molecules for different subsystems.

	Total water		Pure water	Hydration water			
	LiI	KCl		Li^+_{shell}	K^+_{shell}	Cl^-_{shell}	I^-_{shell}
N_H	–	–	–	6.1	7.8	8.2	8.7
O_v	–	–	–	0.13	0.19	0.22	0.27
θ	0.23	0.19	0.18	0.42	0.39	0.29	0.28
AVDIST [nm]	0.289	0.292	0.296	0.266	0.289	0.298	0.303

and KCl, and θ values of hydration water, total water and pure water are presented in Table 1.

It can be seen from Table 1 that O_v decreases with decreasing ionic size, $I^- > Cl^- > K^+ > Li^+$. The average deviation from regular tetrahedrality in pure water is smaller than for total water in the LiI solution but about the same as for the total water in the KCl solution.

In Fig. 1 the distributions of θ for the bulk water in the KCl and LiI solutions are compared with that for pure water. The existence of a shoulder for pure water indicates fluctuations between stronger and weaker tetrahedral arrangement in the liquid. The figure shows that for the KCl solution the distribution is shifted to smaller deviations from regular tetrahedrality and that the shoulder is reduced compared with pure water. This result means that the chloride ion has a similar effect on the bulk water structure as a hydrophobic solute particle [6]. This hydrophobic effect is not compensated by the hydrophilicity of the potassium ion. The distribution of θ for the LiI solution shows that the influence of the Li^+ on the bulk water leads to a more broken structure than in the case of pure water and the KCl solution.

There are extensive discussions in the literature about structure making and structure breaking properties of ions, the main problem being a quantitative measure on a geometrical basis. We suggest the following quantitative measure for the broken structure of hydration water:

$$S = N_H(O_v + \theta_{hydr}) . \tag{8}$$

This definition might be explained by the following arguments. The effect of an ion on water structure consists of three separate phenomena. There is an association of water around the ions in accordance with ion-water interaction (O_v can be used as a quantitative measure of this kind of geometrical structure), a reorganisation of water structure away from regular tetrahedrality as an indirect effect of the influence of ions (θ seems to be a suitable measure for it), and overlap of hydration spheres, which can be neglected for dilute solutions. The values for S calculated according to (8) from Table 1 lead to the following series of structure breaking in the first hydration shell: $Li^+(3.3) < Cl^-(4.2) < K^+(4.5) < I^-(4.9)$. This order is in accordance with the structure breaking order derived from the entropy of hydration, in [6], Table 5.13: $Li^+(-148\,J/(K\,mol) < Cl^-(-87) < K^+(-80) < I^-(-47)$. A quantitative correlation between these entropies and the S values cannot be expected, as in S only the effect of the ions on the structure of the immediate neighbourhood is included. The structural changes beyond the first shell could be reliably calculated only from simulation of solutions of infinite dilution.

The important advantage of the definition introduced here is the opportunity to compute structure breaking as a function of distance from the ions. While O_v has a fixed value for a given ion, θ can be calculated as a function of distance of water from the ion. These functions are given in Fig. 2 for the four ions investigated. In addition, the maxima and minima of the corresponding ion-oxygen RDFs are indicated. It can be seen from Fig. 2 that the θ for the two cations investigated here has reached an asymptotic value already beyond 4 Å. It increases with decreasing ion-oxygen distance. This behaviour is quite different from that of the anions. For both of them θ has maxima (minima) at the first maxima (minima) of the corresponding ion-oxygen RDFs. The strong decrease at short distances can be explained by an increase in the linearity of the water-water bonds. Together with the shorter distances

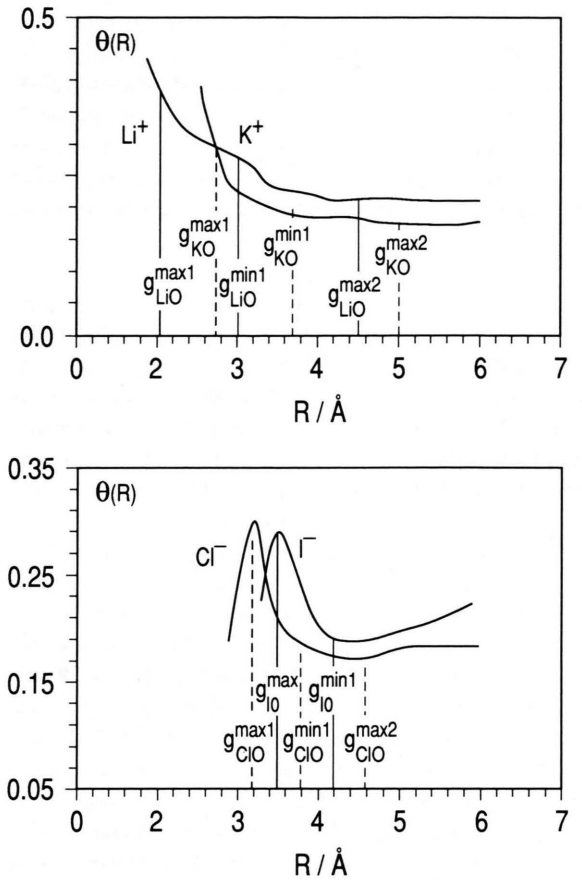

Fig. 2. θ as a function of distance from the ions.

this effect leads to a more pronounced regular tetrahedrality. The orientation of the water molecules in the first hydration shell of the cations is different from that of the anions [13, 15]. The dipole moment points away from the cations. This means that a shortening of the ion–oxygen distance does not improve regular tetrahedrality and θ increases with decreasing distance. The same conclusion has been drawn from an analysis of the hydrogen bonds between water molecules and ions [16]. Besides the angle averaged distance dependence of θ as shown in Fig. 2, it is of interest to see how θ depends on the angle. The visualization of the average distribution of θ in space with respect to an ion and its nearest neighbour would require a four-dimensional representation. We give in Fig. 3 a three-dimensional representation, one dimension for the average θ values and the two other ones for the cartesian coordinates x and y of planes with an ion at the origin and its nearest water molecule on the positive x-axis. Onto such planes we project the θ-values of the water molecules within distances of ± 1.5 Å from the plane, with the exception of the θ value of the nearest neighbour to the central ion, the average of which, the freedom of its position being one-dimensional, cannot be shown in the two-dimensional histogram.

It can be seen from Fig. 3 that for the small lithium ion and the large iodide ion a very clear picture of the deviation from regular tetrahedrality arises from the simulation. For the I^-, in accordance with Fig. 2,

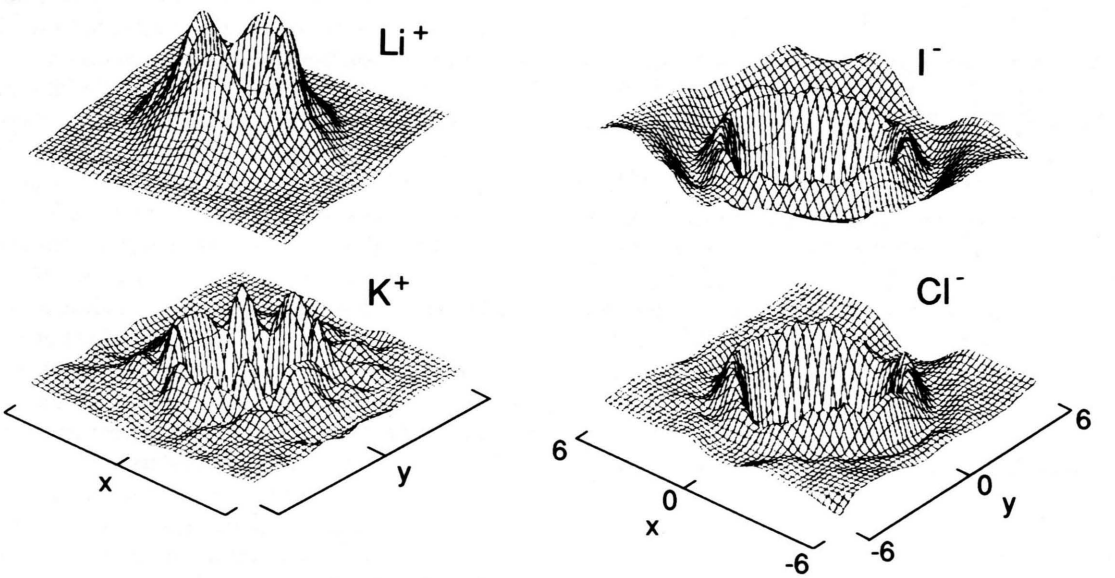

Fig. 3. θ in the neighbourhood of the four ions investigated (for details see text).

θ has a well defined minimum in all directions at a distance immediately beyond the first hydration shell. The height of the maximum of θ at the iodide–water first neighbour distance is also uniform. The result for Li^+ is very different from that of I^-. The octahedral structure of the hydration shell is reflected in the four peaks of θ which correspond to the oxygen atoms of the first neighbour water molecules. The water molecules not occupying vertices of the octahedron, which have usually slightly larger ion–oxygen distances, are less strongly bond and can adjust easier to the energetically more favourable tetrahedral arrangement. A continuous decrease of the tetrahedrality deviation down to the asymptotic value (Fig. 2) can be found in all directions. In the complicated pictures for K^+ and Cl^- features from the relatively easy to understand deviations from regular tetrahedrality for Li^+ and I^- are incorporated. They will not be discussed in detail here.

An interesting problem is the relationship between the local water density and the water structure. Recently, Sciortino et al. [17] investigated the change of structural and dynamical properties with water density. They noted an anomalous behaviour of the self-diffusion coefficient which was found to decrease with decreasing density. The authors showed that a decrease of density leads to an increase of structural order. This result is in accordance with an increase in mobility with increasing pressure [18] which in turn is connected with a decrease in water structure. In analogy we have found that the increase in the distances between the oxygen atoms of the four nearest neighbour water molecules and the central one (AVDIST) for the total water in the LiI and KCl solutions and pure water is connected with a decrease of θ (Table 1). Similarly, the smallest average distances between the water molecules in the hydration shells of the ions correspond to the largest deviation form tetrahedrality, and vice versa, for all ions investigated. The increase in ion–oxygen first neighbour distances leads, for alkali and halide ions, to a decrease in the height of the first peak in the ion-oxygen radial distribution function which means smaller water density in the first neighbour shell. Therefore, the water molecules can arrange, with increasing ion size, in a way which is more bulklike and in which θ decreases.

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[1] J. D. Bernal, Nature London **183,** 141 (1959).
[2] G. Ruocco, M. Sampoli, and R. Vallauri, J. Molec. Struct. **250,** 259 (1991).
[3] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31,** 1164 (1959).
[4] G. Ruocco and M. Sampoli, Chem. Phys. Lett. **188,** 332 (1992).
[5] N. N. Medvedev and Y. I. Naberukhin, Zh. Strukt. Khim. **28,** 117 (1987); see also Y. I. Naberukhin, V. P. Voloshin, and N. N. Medvedev, Mol. Phys. **73,** 917 (1991).
[6] M. G. Kiselev, I. I. Vaisman, Y. P. Puhovski, and Y. M. Kessler, in: Thermodynamics of Electrolyte Solutions (G. Krestov, ed.), Nauka, Ivanovo 1989.
[7] R. J. Speedy and M. Mezei, J. Phys. Chem. **89,** 171 (1984).
[8] P. L. Blumberg, H. E. Stanley, and A. Geiger, J. Chem. Phys. **81,** 5230 (1984).
[9] L. Lamry, Faraday Symp. Chem. Soc. **17,** 79 (1982).
[10] Y. Marcus, Ion Solvation, John Wiley, New York 1985.
[11] M. Mezei, S. Swaminathan, and D. Z. Beveridge, in: Advances in Chemistry, Washington 1983.
[12] K. Heinzinger, in: Computer Modelling of Fluids Polymers and Solids (C. R. A. Catlow et al., eds.), Kluwer Academic Publishers, Dordrecht 1990, p. 357.
[13] J. Seitz-Beywl, M. Poxleitner, and K. Heinzinger, Z. Naturforsch. **46a,** 876 (1991).
[14] G. Jansco, K. Heinzinger, and P. Bopp, Z. Naturforsch. **40a,** 1235 (1986).
[15] M. Poxleitner, Thesis, University of Regensburg, 1991.
[16] Y. P. Puhovski, M. G. Kiselev, I. I. Vaisman, and Y. M. Kessler, in: Thermodynamics of Electrolyte Solutions (G. Krestov, ed.), Nauka, Ivanovo 1992, p. 321.
[17] F. Sciortino, A. Geiger, and H. E. Stanley, J. Chem. Phys. **96,** 3857 (1992).
[18] G. Jancsó, P. Bopp, and K. Heinzinger, Chem Phys. **85,** 377 (1984).