Theoret. Chim. Acta (Berl.) 43, 101–120 (1976)

THEORETICA CHIMICA ACTA

Study of the Structure of Molecular Complexes

XIV. Coordination Numbers for Selected Ion Pairs in Water

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A cluster of 200 molecules of water containing one of the LiF, LiCl, NaF, NaCl, KF or KCl ion pairs has been studied at the temperature $T = 298^\circ$K using Monte Carlo techniques. The anion-cation internuclear separations considered in this work for any of the above pairs are 6.0 Å, 8.0 Å and 10.0 Å. The water-water potential is obtained from quantum-mechanical Hartree-Fock type computations corrected by inclusion of dispersion forces; the ion-water potentials have been obtained from Hartree-Fock type computations on the single ion-water complex. The computed radii for the first hydration shell are 2.7 ± 0.1 Å, 3.4 ± 0.3 Å, 4.0 ± 0.3 Å, 3.0 ± 0.5 Å, and 3.9 ± 0.4 Å, for Li^+, Na^+, K^+, F^- and Cl^-, respectively. The computed coordination numbers are 5.4 ± 0.7, 6.0 ± 1.1, 7.2 ± 1.2, 4.5 ± 0.6 and 5.1 ± 0.8 for the same ions, respectively. The range of the coordination number obtained from compressibility, enthalpy, NMR spectroscopy and other experimental methods is much larger than the error ranges above given. Therefore the Monte Carlo simulation provides reliable information on the cluster shape, cluster structure and on the coordination numbers and hydration shell radii for the cations and anions, when both are present in a water cluster.

Key words: Ion pairs in water, coordination numbers

1. Introduction

In previous papers [1], we analyzed the structure of a cluster of 50 and 200 molecules of water containing the LiF ion pair. In this paper we continue the analysis, with the emphasis on a systematic comparison for the LiF, LiCl, NaF, NaCl, KF and KCl ion pairs when surrounded by a large number of molecules of water (200 molecules) at room temperature (298°K).

An early two-body Hartree-Fock potential [2] for the water-water interaction is in error because of neglect of the electronic correlation corrections. Further, an improved two-body Hartree-Fock potential [3], obtained by a more extensive sampling of the potential surface, still retains (by definition) the above limitation. Both potentials have been extensively tested in determining the pair correlation functions for liquid water [2, 4]. The electronic correlation correction, which is of interest here since it amounts to about 40% of the water-water binding, can be estimated [4] with a number of approximations, like the Kirkwood-Müller [5] or the London [5] or the Wigner-type correction [6]. More recently, computations made by the Warsaw Theoretical Chemistry Group [7], using perturbation techniques, have narrowed considerably the range of uncertainty for the electronic correlation corrections[1]. Such corrections have here been introduced in a way as to affect mainly the radial part of the potential, i.e., configurations with different oxygen-oxygen distances. The angular part, i.e. the *orientation* of the two molecules at a *given* oxygen-oxygen distance, is not known but, fortunately, the radial part applies to that orientation which is in the lowest energy state.

Thus the two-body Hartree-Fock plus dispersion force potential, hereinafter referred to as the (HF + D) potential, is used in this work. It has been tested in a theoretical study of the pair correlation function for the oxygen-oxygen, oxygen-hydrogen and hydrogen-hydrogen pairs and experimentally tested in reproducing the neutron as well as X-ray scattering intensity spectrum for liquid water [8]. Comparison with experimental neutron-scattering and X-ray scattering intensities reveals that the (HF + D) potential is superior to the above referenced Hartree-Fock potentials alone.

With reference to Fig. 1a, the water-water potential used in this paper has the form:

$$\begin{aligned}E= {} & q^2(1/r_{13} + 1/r_{14} + 1/r_{23} + 1/r_{24}) + 4q^2/r_{78} - 2q^2(1/r_{18} + 1/r_{28} + 1/r_{37} + 1/r_{47}) \\ & + a_1 \exp(-b_1 r_{56}) + a_2 [\exp(-b_2 r_{13}) + \exp(-b_2 r_{14}) + \exp(-b_2 r_{23}) \\ & + \exp(-b_2 r_{24})] + a_3 [\exp(-b_3 r_{16}) + \exp(-b_3 r_{26}) + \exp(-b_3 r_{35}) \\ & + \exp(-b_3 r_{45})] + \frac{c_1}{r_{56}^6} - \frac{c_2}{r_{56}^8} + \frac{c_2}{r_{56}^{10}}\end{aligned}$$

The set of constants used in the present work (in Å. and Kcal/mole) are:

$q = 139.272$ $a_1 = 71533.4$ $a_2 = 779.885$ $a_3 = 4084.02$

$b_1 = 3.96994$ $b_2 = 3.12544$ b_3 3.91443

$c_1 = 922.781$ $c_2 = 17283.5$ $c_3 = 24119.7$

The subscript 7 corresponds to a point on the symmetry axis which is 0.225954 Å

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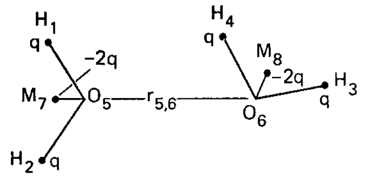
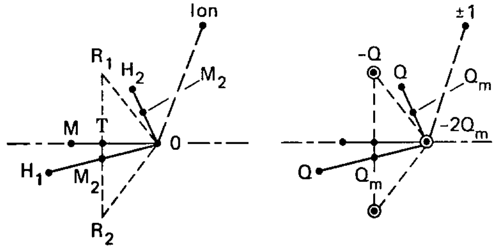
[1] A high accuracy potential using a very large number of configuration interaction techniques computed for a large number of water-water geometries is under study (Matzuoka, O., Yoshimine, M., Clementi, E.: to be published). Preliminary use of this potential, when applied to the problem of liquid water, indicates a very high degree of reliability in accurately reproducing the experimental X-ray and neutron diffraction intensities (Lie, G. C., Clementi, E., Yoshimine, M.: J. Chem. Phys. **64**, 2314 (1975).



(a) Water–Water Model

Fig. 1. Point charge model used for the analytical fitting to the Hartree-Fock numerical results for the $(H_2O)_2$ complex and for the (ion–water) complex at many geometrical configurations. Such models have been extensively discussed in previous publications (see Refs. [2–4, 9]



(b) Water–Ion Model

away from the oxygen atom of the first water molecule. The subscript 8 is similarly defined with respect to the second water molecule. The O-H distance is 0.957 Å. The position and sign of the point charges are explained in Fig. 1a.

For the ion–water interaction potentials, there exists a systematic study using Hartree-Fock potentials derived for the complexes of one water molecule with one of the ions Li^+, Na^+, K^+, F^- and Cl^- [9]. These two-body Hartree-Fock potentials have been corrected using a Wigner-type statistical model in order to estimate the correlation energy correction; we note that the correction is small and, in practice, negligible, since the main contribution to the water–ion binding energy is of ionic character, and, therefore, can be represented with sufficient accuracy in the Hartree-Fock approximation. The pair potentials used in this paper to describe the cation–water and anion–water interaction have the form:

$$E = Q(R^{-1}_{I-H_1} + R^{-1}_{I-H_2} + R^{-1}_{I-R_1} + R^{-1}_{I-R_2}) - Q_m(R^{-1}_{I-M_1} + R^{-1}_{I-M_2} + 2R^{-1}_{I-O})$$
$$+ a_1\,[\exp(-a_3R_{I-H_1}) + \exp(-a_3R_{I-H_2})] + a_2\exp(-a_4R_{I-M})$$

The values of the numerical constants appearing in the above equation are reported in Table 1, and the position of the point charges Q and Q_m are explained in Fig. 1b (the subscript I refers to the position of one of the ions in the pair regardless of its sign). In the potential that describes the water–ion interaction, the O-H distances are 0.975 Å and the O-M distances are half this, i.e., 0.4785 Å. The H_1-O-H_2 angle is taken as 104.87.

The two potentials given represent a good fit to Hartree-Fock computation for water dimer [8] and single ion–water complexes (for further discussions on the potentials we refer to the original papers [2–4, 9]).

Table 1. Optimized parameters for ion–water potential (in kcal/mole, and Å)

	Li^+	Na^+	K^+	F^+	Cl^-
Q	212.31184	196.64883	197.78442	−216.65836	−204.09683
Q_m	20.56076	21.80928	16.918137	9.5963516	42.164169
a_1	4739.2188	117717.13	2795.3428	2682.6250	3806.5325
a_2	41906.387	123043.44	234552.81	131805.75	43682.949
a_3	6.7123232	7.4594021	4.9926376	3.762742	3.0973005
a_4	4.4961967	4.4644489	4.0884628	4.3881969	3.3054581
$\overline{OM}$	0.0208333	0.0179123	0.042201	0.0816980	0.14916152
$\overline{OT}$	0.1378797	0.1399276	0.186526	0.22380584	0.24730611
$\overline{TR}_1$	0.0029527	0.095599	0.00713105	0.15092367	0.11294532

We have previously commented on some features of the Monte Carlo program we have used [1] ; the original version of the program, written by R. O. Watts, has been improved in order to gain efficiency, by J. Fromm; a rather extended documentation of the improved version has recently been written [10].

The main saving introduced in Fromm's version of the Monte Carlo program is obtained by considering two regions for the potentials in the water-water interactions. The full potential, as given in the previous section, is used for relatively short and medium distances, a simpler form, neglecting the exponential terms, is used for distances larger than a pre-established threshold (7 Å).

Typically the computation of $1 \cdot 10^5$ configurations, for a cluster of 200 molecules of water, requires about 4 hours on an IBM 370/168 computer.

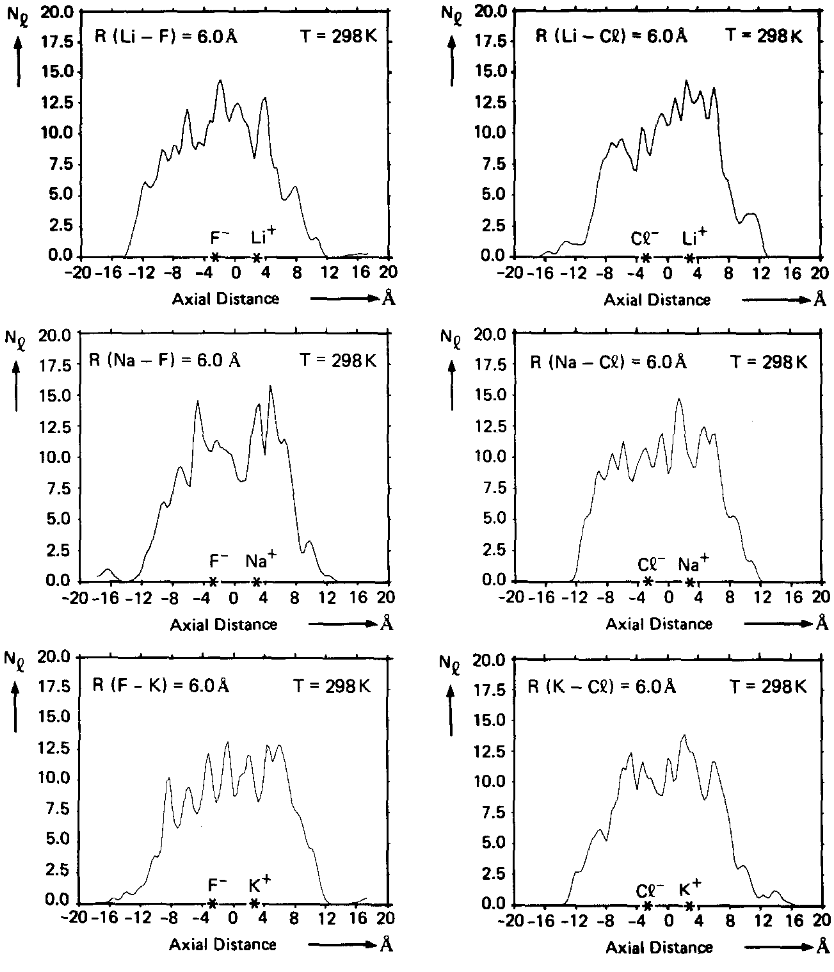


Fig. 2. Cluster envelope projected on the x-axis for the whole set of ion pairs. The position of the ion pair is marked on the x-axis. The distance between the ions is 10.0 Å

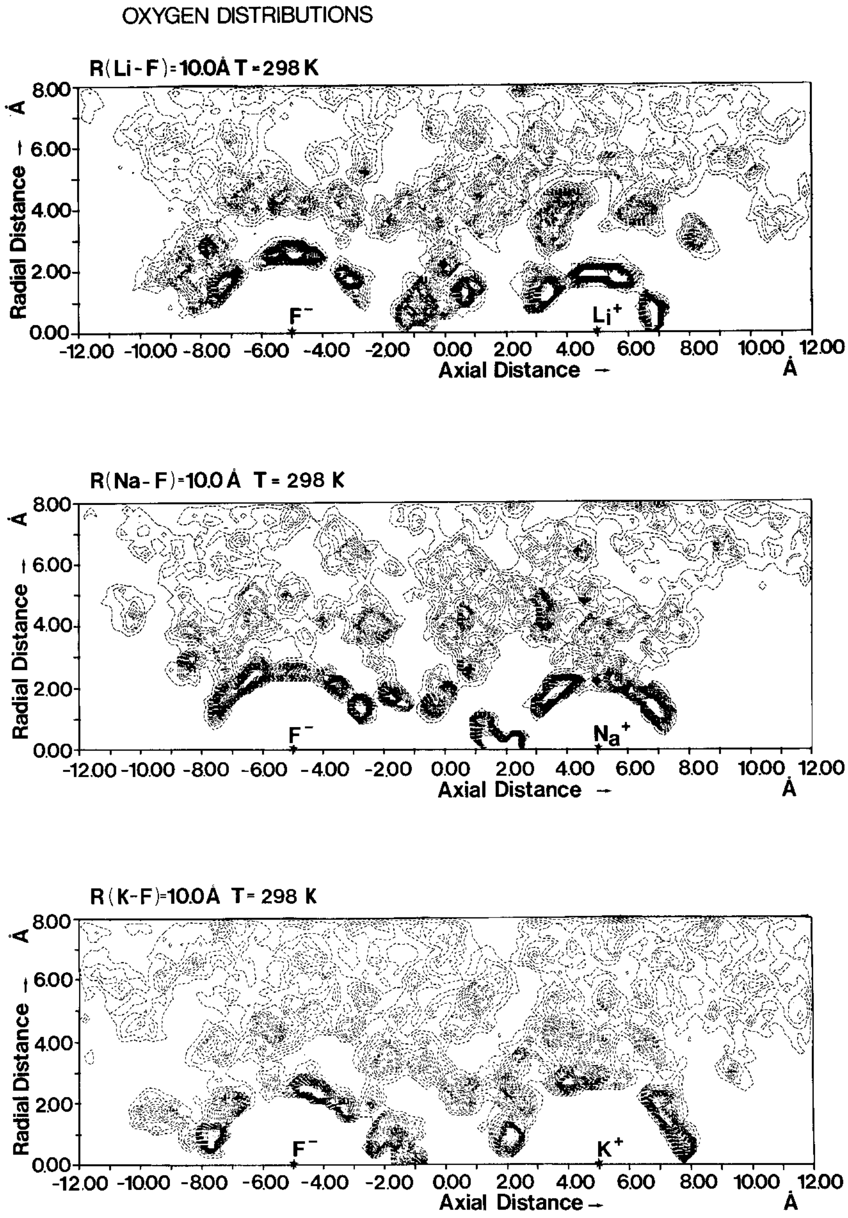
2. Shape of the Cluster

Three different interionic distances have been selected for each ion pair. Constraining the two ions on the x-axis, these are 6.0 Å, 8.0 Å, 10.0 Å. In all cases the mid-point of the anion–cation separation have been selected at $x = 0.0$; in addition the anion has been placed at the left of the cation, namely the anion is either at $x = -3.0$ Å, or $x = -4.0$ Å, or $x = -5.0$ Å.

In Fig. 2 the overall structure of the clusters is represented by reporting the statistical average of the population of the atoms at various positions along the x-axis for the case of an interionic distance of 10.0 Å (equivalent figures for the interionic distances of 6.0 Å and 8.0 Å are available from a Technical Report - Donegani, June 27, 1975).

The vertical scale is such that $10N_1 \rightarrow N_1$ is the number of molecules per unit length. For all cases, the cluster center appears to be unsymmetrically displaced along the x-axis and no striking regularity can be detected either by comparing different ion pairs at the same anion–cation separation or by comparing, for a given ion pair, different anion-cation separations. We find that the length of the cluster along the x-axis increases with increasing distance of the two ions, but this feature is clearly expected. In addition we note that for the case of NaCl the cluster's left and right boundaries are more symmetrically located than in any other case. In the case of NaF a cleavage can be detected which is more strongly marked than in the case of the other two fluorides at any distance. The cluster character is retained at all interionic distances at the chosen temperature, namely there is a very well defined beginning and a very well defined end at the two extremities of the cluster. The fine structure of the cluster is another general characteristic that emerges from the probability distribution reported in Fig. 2. This fine structure, having an interval, from maximum to maximum, of about 3 to 4 Å, indicates that the whole system of 200 molecules of water and the two ions is *highly structured* even at room temperature. Three-dimensional pictures obtained by video display of a number of specific configurations, rather than by considering the statistical distribution of the water molecules, reveals "filaments" of water molecules, where one molecule is hydrogen bonded to the other, departing from the ions and extending towards the cluster surface. The fine structure of the cluster is due to these filaments, or polymers, of the water.

Since this feature has been noted over and over, either using different potentials [1] or different temperatures [2] or different ions, we are of the opinion that it represents a real feature of the water organization around ions, and with a reasonable extrapolation, around ionic groups (for example a carboxylic group). Considering the water arrangement about ions, one traditionally talks about hydration shells. Equally reasonably one could talk of water polymers departing radially from the ion and having a characteristic length and a stability that decreases with increasing distance from the point charge at the ion. After a given number of units (water monomer) the order introduced by the ionic field (reflected in the water polymer formation) is counter-balanced by the thermal motion (disorder) of the liquid. The concept of solvation shell in part originates from considering the liquid water as a continuum medium, and therefore neglecting to some extent the molecular aspect of the water molecules in the liquid. The concept of water polymers can help a complementary description in restating the molecular, the geometrical and the discrete aspect of the liquid. After all, to insist that 4 to 8 points (the oxygen positions for the water molecules in a given shell) define a sphere, and only a sphere, is perhaps a point of view a bit too rigid and dogmatic.



OXYGEN DISTRIBUTIONS

R(Li-F)=10.0Å T=298 K

R(Na-F)=10.0 Å T = 298 K

R(K-F)=10.0Å T= 298 K

Fig. 3. Oxygen distribution contour map for the most relevant region of the cluster. The maps are relative to the ion pairs LiF, NaF and KF at an interionic separation of 10.0 Å

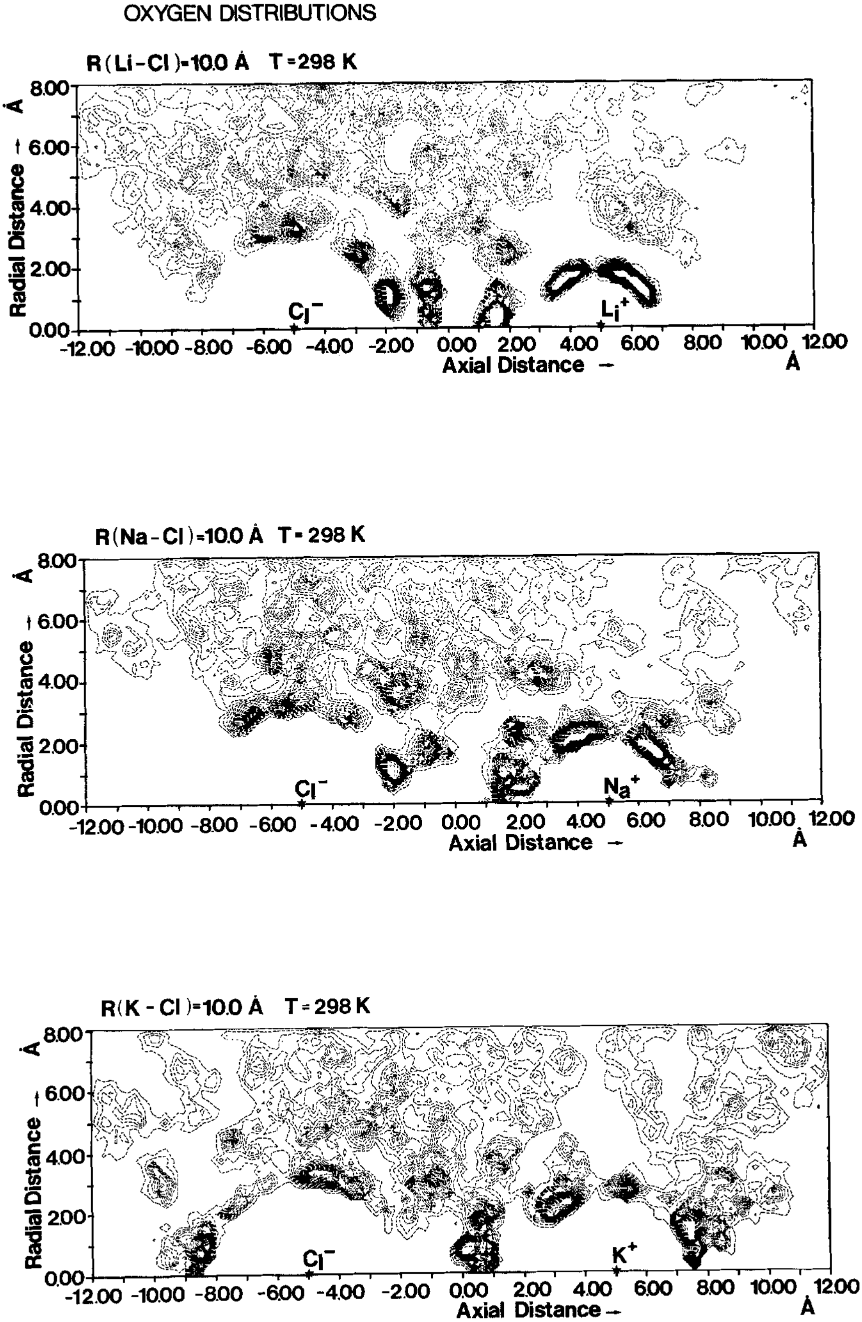


Fig. 4. Oxygen distribution contour maps for the most relevant region of the cluster. The maps are relative to the ion pairs LiCl, NaCl and KCl at an interionic separation of 10.0 Å

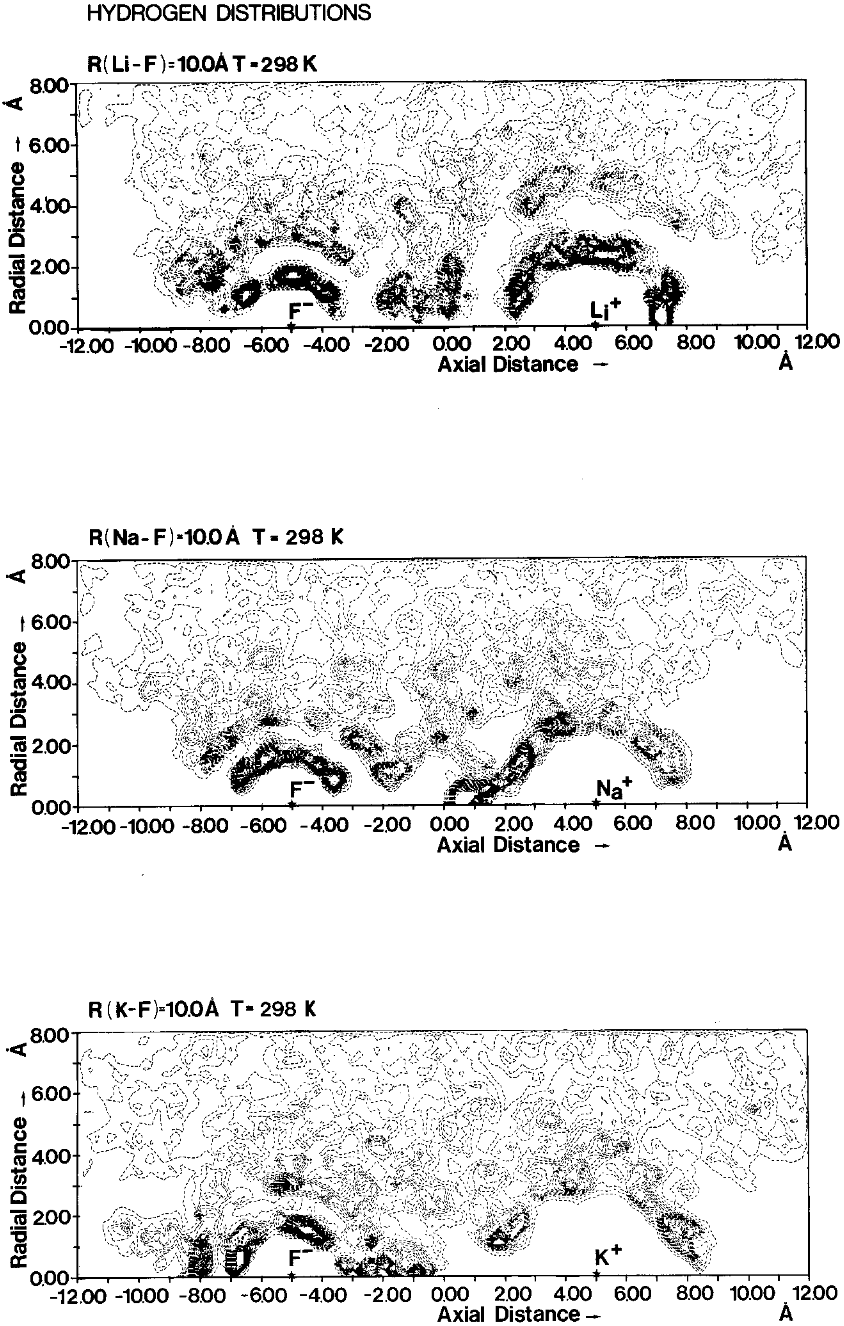


Fig. 5. Hydrogen distribution contour maps for the most relevant structure of the cluster. The maps are relative to the ion pairs LiF, NaF and KF at an interionic separation of 10.0 Å

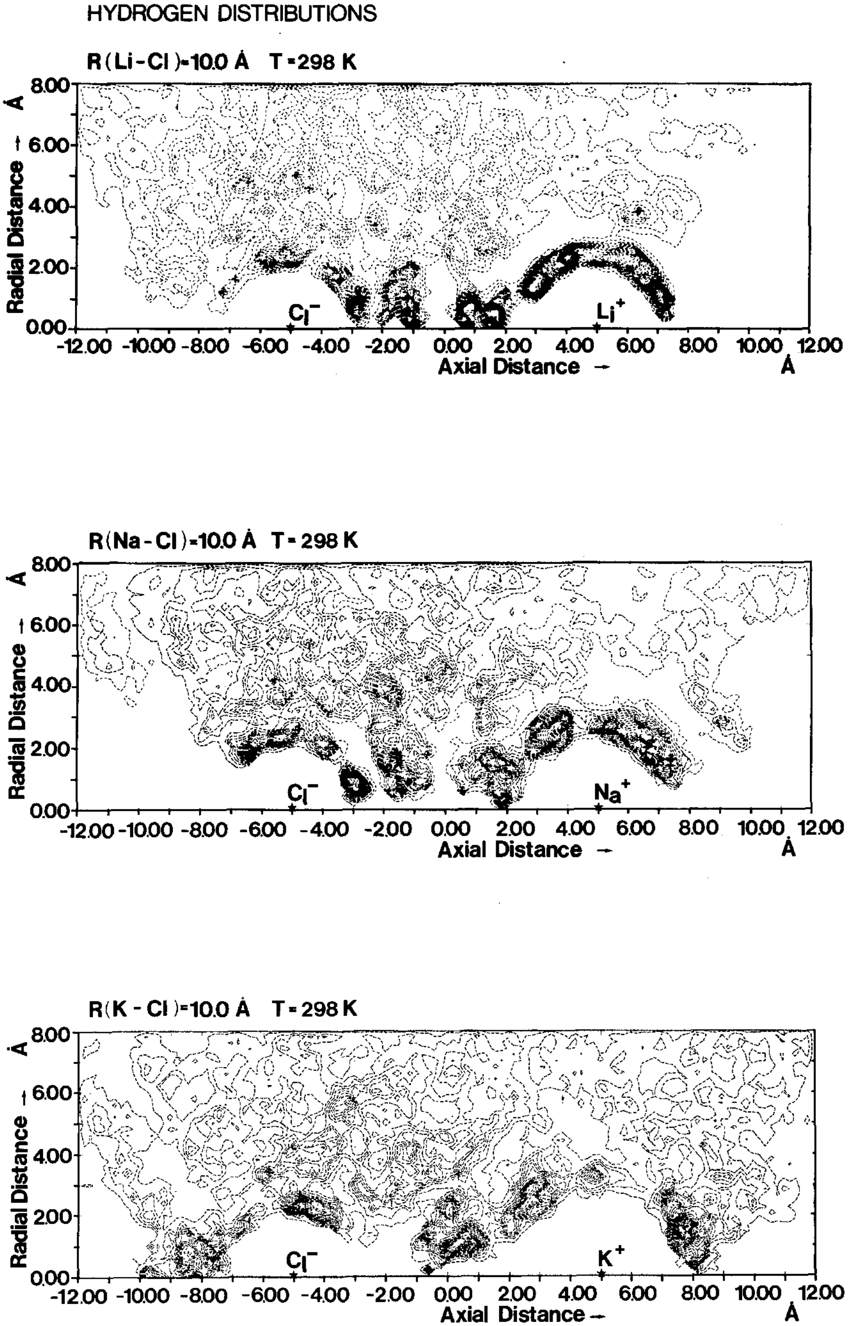


Fig. 6. Hydrogen distribution contour maps for the most relevant structure of the cluster. The maps are relative to the ion pairs LiCl, NaCl and KCl at an interionic separation of 10.0 Å

3. Structure of the Cluster

The radial distribution functions of interest in the cluster studies are those for the positive or negative ion (i) and for the hydrogen or oxygen atoms (A), namely

$$f_i^{\mathrm{A}}(x, r) = \frac{\langle N_i\{(x, x + \delta x),(r, r + \delta r)\}\rangle}{2\pi r \delta x \delta r}$$

where the oxygen (or hydrogen) is in the range $(x, x + \delta x)$ and within $(r, r + \delta r)$ of the axis; $(r^2 = y^2 + z^2)$. For additional explanation we refer to the previous work [1].

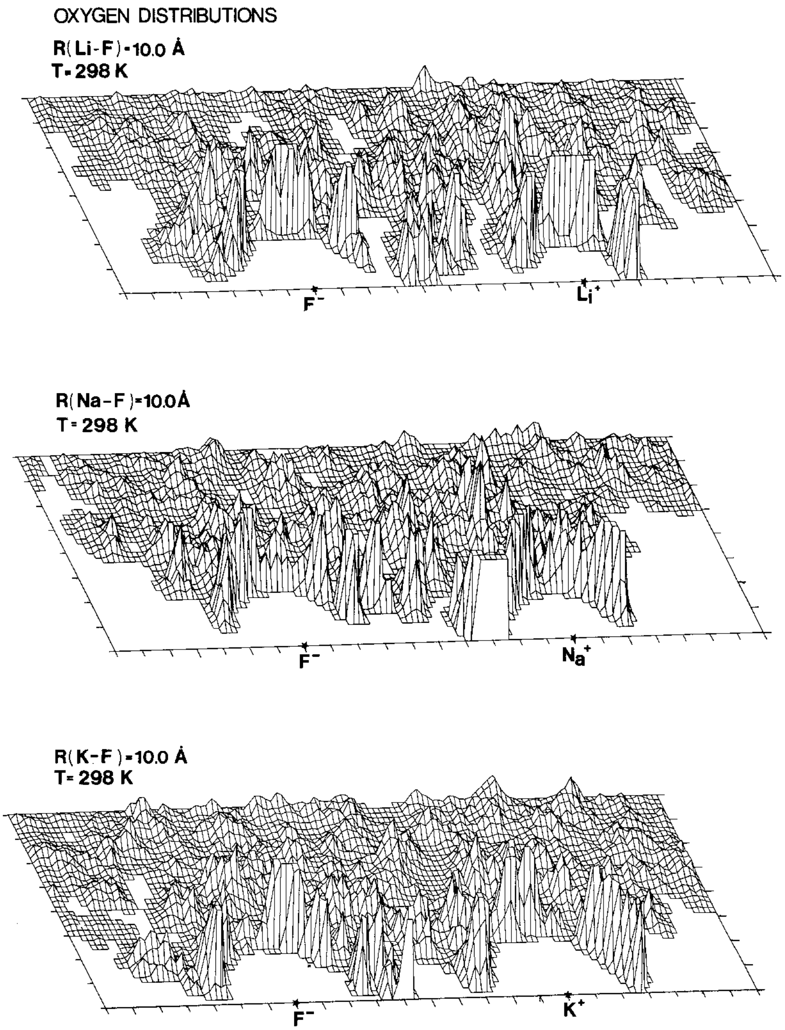


Fig. 7. Oxygen distribution: three-dimensional representation. The data of this figure are equivalent to those of Fig. 3 but differently displayed

Figs. 3 and 4 report the contour, probability plot for the oxygen distribution, $f_i^{O}(x, r)$ Figs. 5 and 6 the contour plot for the hydrogen distribution, $f_i^{H}(x, r)$, and Figs. 7 and 8 give the same data as Figs. 3 and 4, but in a three-dimensional form to facilitate unde standing of the cluster structure. The contour intervals (Figs. 3 and 4) are 0.02 atoms $Å^{-3}$. There is not only evidence of a first hydration shell, but also of a second hydratio shell. This detail was less evident in the 50 molecules simulation [1a]. In Figs. 7 and 8, the area considered is the same as in Figs. 3 and 4: the tic marks at the perimeters are for intervals of 1 Å, as in Figs. 5–10.

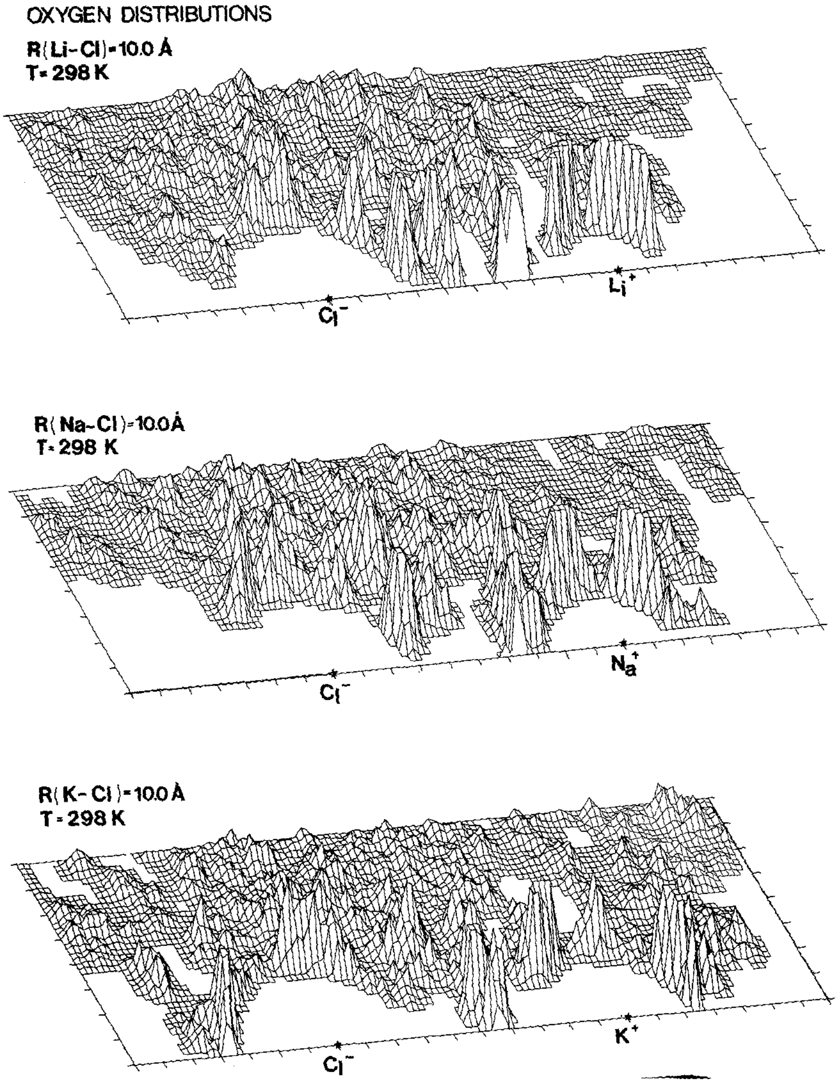


Fig. 8. Oxygen distribution: three-dimensional representation. The data of this figure are equivalent to those of Fig. 4 but differently displayed

We wish to emphasize that all the data presented in Figs. 3 and 4 are obtained by considering only 3 x 10^5 configurations *after* we have reached convergency in the Monte Carlo simulation [1]. In this way the data shown in the figures represent a relatively small statistical sampling of configurations (3 x 10^5), and this sampling is influenced

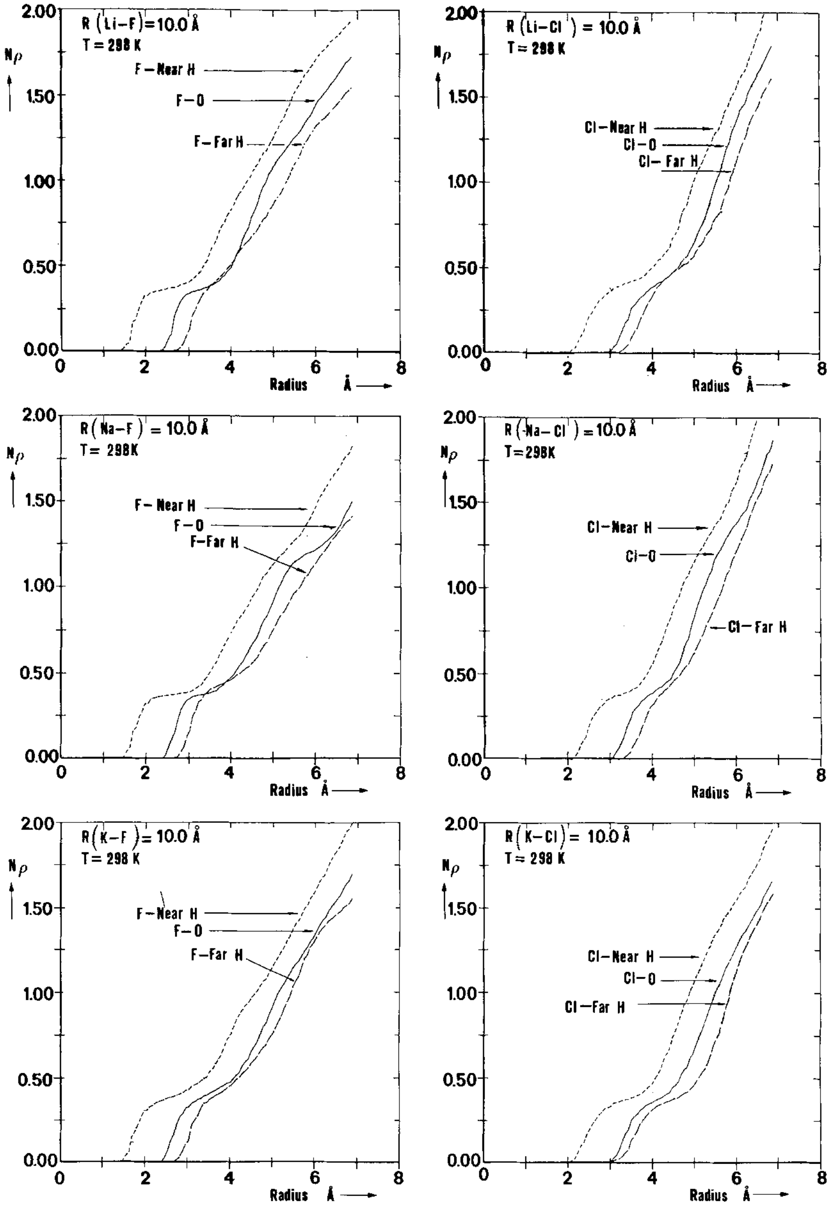


Fig. 9. Integral of local density for each of hydrogens of water and for the oxygen relative to the anion placed at the origin. The six pictures are relative to the whole set of ion pairs at an interionic separation of 10.0 Å

by the starting configuration, the last obtained in order to reach convergency. In this way a number of low-probability configurations might be included and, correspondingly the probability peaks are very sharp and localized. In other words, the results reported represent a *portion* of the entire statistic we have considered, namely a portion in the neighbourhood of the maximum of probability. In these figures we have attempted to balance two extreme situations: if we report the data for *very few* configurations (say 30), taken after we have reached convergency in the Monte Carlo sense [1], we could show much greater *molecular* details, indeed a clear localization of all the 200 molecules of water, but these details would have a marginal statistical relevance; if, on the other hand, we report the data for *many configurations* (say 3×10^6), taken after having reached convergency in the Monte Carlo sense, we will have lost in the figures much of the molecular details but gained in *statistical* relevance.

In the reported figures we have chosen a compromise attitude; for this reason the graphs in Figs. 3 and 4 might give a deceptive impression that either the water molecules have a very localized distribution or that all the points of the configuration space have not been equally weighted.

4. Coordination Numbers

The simplest and somewhat naive definition of the coordination number for a given ion in aqueous solution is simply the number of water molecules that surround that ion within a defined volume, for example a sphere, having the ion at its center. A more physical definition should express the relationship of the coordination number with temperature and with the presence or absence of other ions. In this work we have presented a number of computer experiments (all done at the same temperature) where we have obtained the statistical distribution of water molecules around a pair of ions, at various interionic separations. We shall now make use of the result of our computational experiments and attempt to determine the coordination numbers of the Li^+, Na^+, K^+ cations and of the F^- and Cl^- anions.

We can integrate over the space coordinates for the correlation functions $f_i^O(x, r)$ and $f_i^H(x, r)$ previously defined, the integration is for a volume having the ion (indicated by the subscript i) as its center. The function obtained by integrating $f_i^O(x, r)$ from $r = 0$ to a finite value is designated as N_O, and the function obtained by integrating $f_i^H(x, r)$ from $r = 0$ to a given value is designated as N_H. Clearly, N_H and N_O can be used as a definition and for the determination of the coordination numbers, since the function N_H or N_O corresponds to the number of hydrogen atoms or to the number of oxygen atoms contained in a defined spherical volume having the ion as origin. In Fig. 9 we report N_H and N_O for the negative ions F^- and Cl^- in the presence of a given counterion computed for the different ion-pair separations previously discussed. Since for the negative ion one of the hydrogen atoms of a water molecule is hydrogen-bonded to the anion, we report two curves for N_H, one corresponding to the hydrogen atom nearer to the anion (hydrogen-bonded), the second for the hydrogen atom further away and not hydrogen-bonded to the anion. In fig. 10 we report the values of N_H and N_O for the Li^+, Na^+ and K^+ cations in the presence of F^- or Cl^-; in this case, since the hydrogen atoms are not hydrogen-bonded to the cations, we report only one function for the

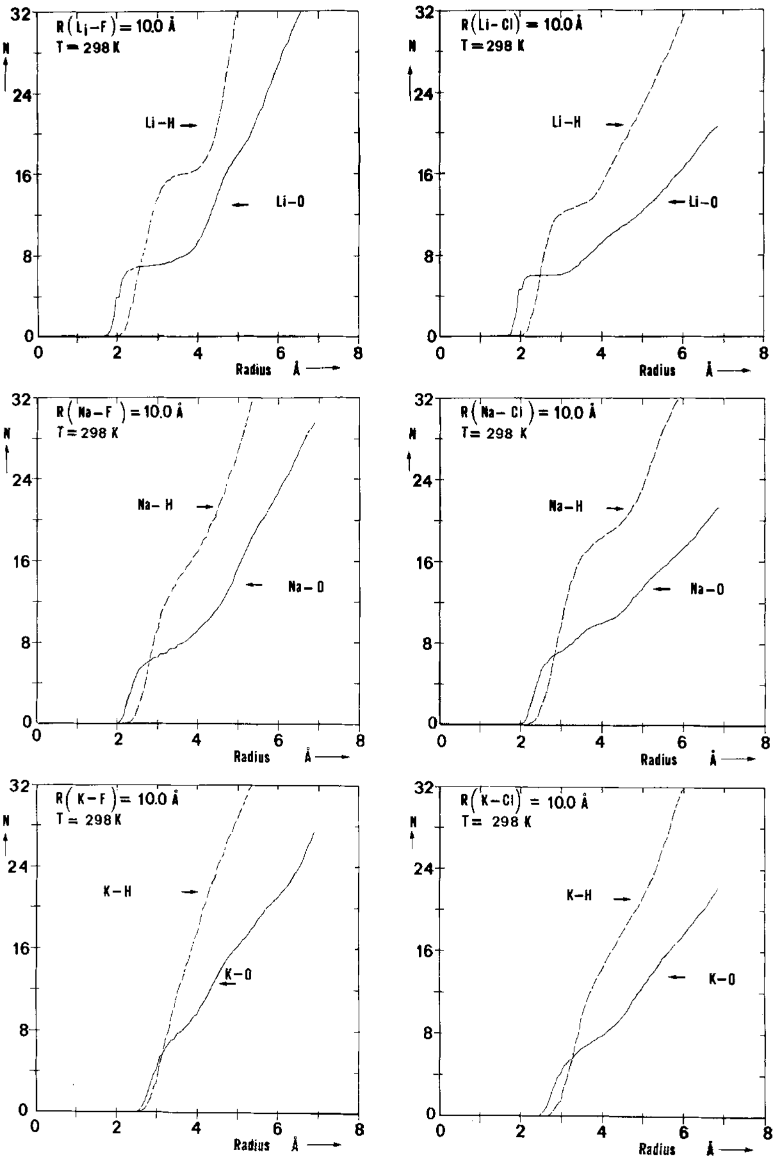


Fig. 10. Integral of local density for the sum of the two hydrogens of water and for oxygen atoms relative to the cation placed at the origin. The six pictures are relative to the whole set of ion pairs at an interionic separation of 10.0 Å

hydrogen atoms distribution. It should be pointed out, however, that a difference in the probability distribution for the two hydrogen atoms of a water molecule can be detected in some of the reported graphs describing $N\rho$ for hydrogen atoms around positive ions; in particular, for the case of the Li^+ cation a splitting of the maximum probability peaks can be noticed. On the other hand, we feel that it is simply an effect due to the presence of the anion in the ionic pair studied, since the effect is more pronounced the nearer the interionic separation.

Since a plateau for a given range of r in the N_H and N_O curves indicates that the integral value remains constant for that range of r, the detection of such a plateau is an indication that a "hydration shell" is completed and thus provides us with a quanti-

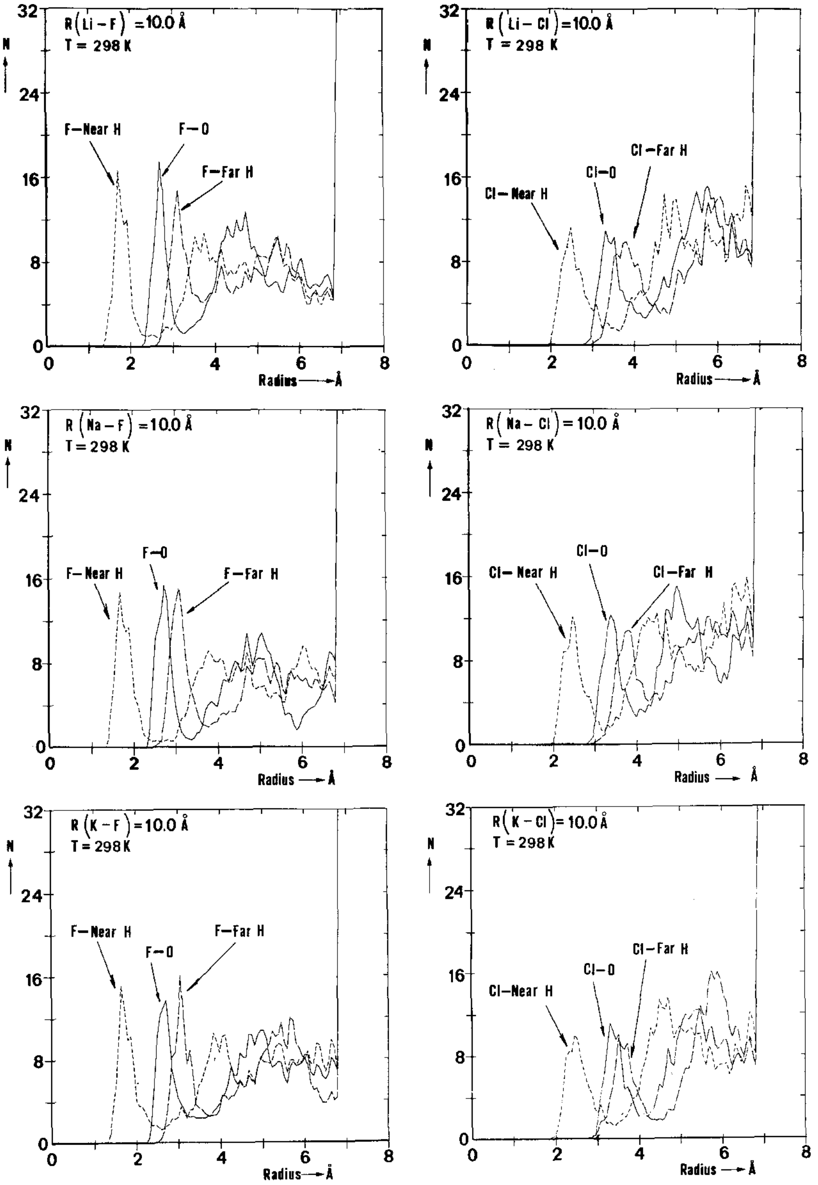


Fig. 11. Derivatives of the local density distributions given in Fig. 9

tative value of the hydration shell radius. Thus, in principle, from the graphs of N_H and N_O we could obtain both the coordination numbers and the shell radius. From inspection of Figs. 9 and 10 it appears, however, that it might not be sufficiently clear how to determine the radius. Therefore we report in Figs. 11 and 12 the derivatives of

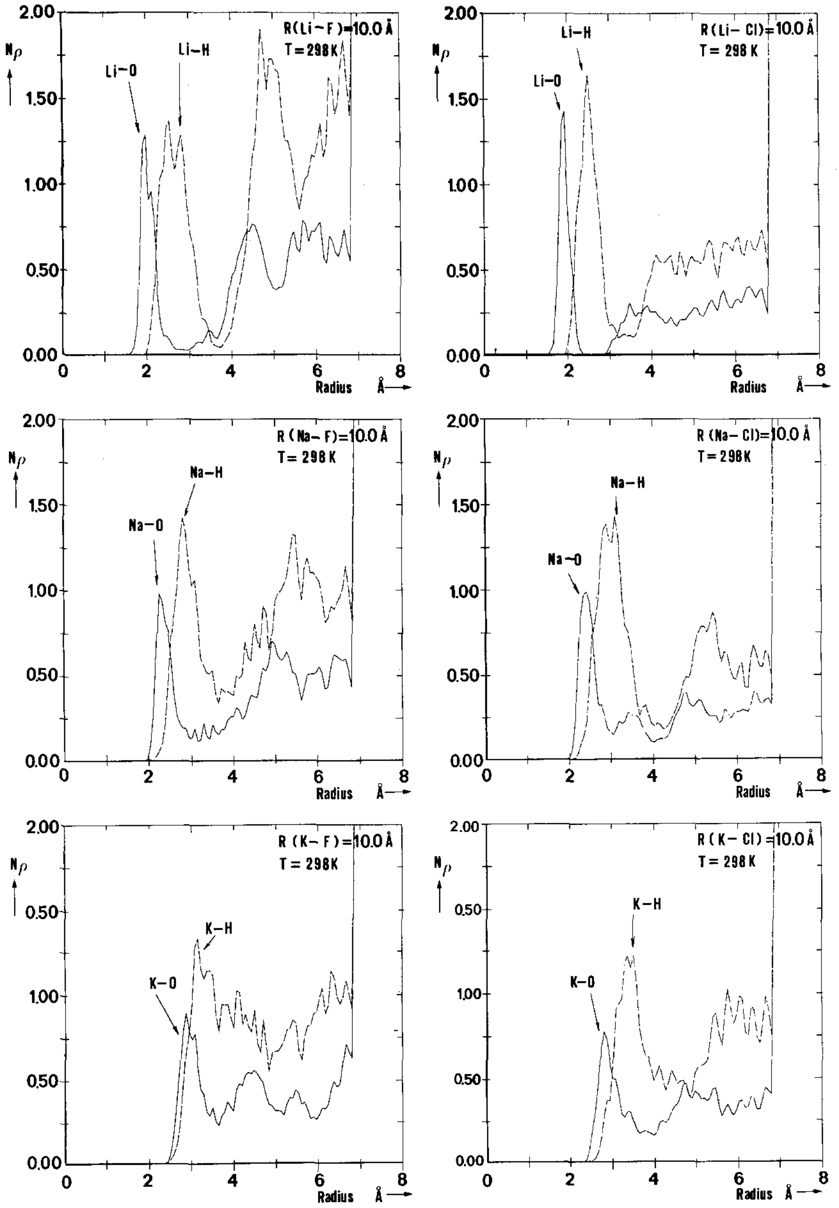


Fig. 12. Derivatives of local density for the sum of the two hydrogens of water and for oxygen atoms relative to the cation placed at the origin. The six pictures are relative to the whole set of ion pairs at an interionic separation of 10.0 A

N_H and N_O; indicated as $N\rho$ the vertical scale is such that $N\rho/4\pi r^2(\Delta r)$ is in molecules per unit volume (Å^3). From Figs. 11 and 12 we can obtain the radii of the first and second hydration shells in a simple way. *First*, we must realize that a shell has an intrinsic thickness, therefore it is defined by an initial radius (inner edge) and a final radius (outer edge). The initial radius corresponds to a maximum in Figs. 11 and 12 of a given distribution, the final radius corresponds to the minimum of the same distribution; therefore we can define an average radius as the arithmetic mean of the initial and of the final radius. Once the radius is determined the computation of the coordination numbers is immediate, since it can be read directly from the data in Figs. 9 and 10. *Second*, one can distinguish between the anions and the cations; for the anions there is a distinct distribution for the inner hydrogen (hydrogen-bonded) and for the outer of H_2O; for the cation the two hydrogen distributions are over-imposed. Thus in this work, to properly interpret our simulated data, we must consider a shell as an organized structure having a finite thickness, where the shell is properly defined; between shells there is a region of statistically rather disordered structure. The coordination numbers are, as usual the numbers of molecules of water in the volume defined by the shell radius. For example in the case of Li^+ (see Table 2) the organized structure of the first shell is within two radii of 2.2 Å and 3.3 Å (giving an average of 2.7 Å). The second shell is statistically well-defined from a radius of 4.7 Å to a radius of 6.2 Å; in the region 3.3 Å to 4.7 Å the density distribution is low and statistically poorly defined (note that the thickness of a shell, defined as the interval between the two radii, is of the order of about 1 Å for cations, and larger for the anions, as expected on hydrogen-bond considerations.

Table 2. Coordination numbers and hydration shell's radii (Å) for selected ions[a]

	First Shell		Second Shell	
Ion	Radius (A)	Coordination	Radius	Coordination
Li^+ I	2.2 ± 0.1	4.7 ± 0.4	4.7 ± 0.2	9.3 ± 0.5
O	3.3 ± 0.2	6.2 ± 1.0	5.5 ± 0.6	18.5 ± 4.9
Av	2.7 ± 0.1	5.4 ± 0.7	5.1 ± 0.4	13.9 ± 2.7
Na^+ I	2.8 ± 0.2	4.6 ± 0.6	5.2 ± 0.2	13.2 ± 2.0
O	4.0 ± 0.4	7.4 ± 1.6	6.6 ± 0.5	21.2 ± 3.2
Av	3.4 ± 0.3	6.0 ± 1.1	5.9 ± 0.3	17.1 ± 2.8
K^+ I	3.5 ± 0.2	4.4 ± 0.8	5.4 ± 0.3	12.6 ± 4.0
O	4.5 ± 0.4	10.0 ± 1.6	–	–
Av	4.0 ± 0.3	7.2 ± 1.2	(5.4 ± 0.3)	(12.6 ± 4.0)
F^- I	2.0 ± 0.4	3.0 ± 0.6	4.0 ± 0.2	12.0 ± 0.8
O	3.3 ± 0.6	6.0 ± 0.8	5.5 ± 0.6	18.8 ± 2.6
Av	3.0 ± 0.5	4.5 ± 0.7	4.7 ± 0.4	15.4 ± 1.7
Cl^- I	3.0 ± 0.4	4.8 ± 0.6	5.9 ± 0.4	15.7 ± 1.0
O	4.5 ± 0.6	5.5 ± 1.0	6.5 ± 0.6	20.1 ± 3.9
Av	3.9 ± 0.5	5.1 ± 0.8	6.2 ± 0.5	17.9 ± 2.4

[a] The initials I, O, Av designate the values at the inner edge of a shell, at the outer edge, and the average value.

Equivalently we can define the radius of the second hydration shell. However, in this case some additional care must be taken due to the fact that we have considered finite interionic distances. For a given radius of the volume surrounding an ion (e.g. the anion) the water included in the sphere not only "belongs" to that ion but might belong, in addition, to the second ion (e.g. the cation). This is a difficulty we encounter in unambiguously defining the coordination number of ions in clusters containing two ionic species (clearly for highly diluted solutions this problem does not arise, since the solvation shells do not overlap).

In order to avoid this ambiguity we define the coordination numbers by limiting the integration of the function $f(x, r)$ to the volume either to the left (for the cation) or to the right (for the anion) with a perpendicular to the x-axis (the interionic axis) and bisecting it at $x = 0.0$ Å. In this way the ambiguity is removed to a large extent.

In Table 2, we summarize the values obtained with the above procedure for the radii and coordination numbers of the first and second shells.

From the data in Table 2, we notice that the errors in the determination of the radius are relatively small (up to 10%) with the exception of the K^+ cation, where we have not been able to clearly determine the radius of the second hydration shell. The error in the determination of the coordination number is between 10% and 25%, i.e., much less precisely determined than the radii. One of our aims for this work was to study the influence on the coordination numbers and radii of the second ion in the ion-pair situation; the error limit of our computation is too large to see such effect. Thus we can preliminarily conclude that the perturbation of the second ion is smaller than the above-given errors for ion–ion distances larger or equal to 8 Å.

A comparison with experimental determinations of the coordination number reveals that our conclusions are quite useful since all experimental determinations depend heavily on the models that are assumed for the solvent around the ion, and none are direct determinations of the number of molecules around a small volume element of solvent.

For the Li^+, Na^+ and K^+ ions the coordination numbers experimentally reported are 4.5, 4.5 and 3.8, respectively (compressibility data [11]), 5, 4 and 3, respectively (entropy data [11]), 2.5, 4.8 and 1.0, respectively (density data [13]), 5.5, 7.0 and 6.0, respectively (compressibility data [14]), 5 ± 2, 3 ± 1.2, and 1 ± 0.4, respectively (NMR data [15]), 3.4, 4.6, and 4.6 (NMR data [16]). This extended spread of "experimental data" for the cations is similar to what is reported for the anions: for F^- and Cl^- the reported experimental coordination numbers are 4.0 and 2.2 respectively (compressibility [11]), 5 and 3 (entropy [12]), 2.0 and 1.0 respectively (compressibility [14]), 9.9 ± 2 and 13.2 ± 2 (NMR data [17]). This list of experimental numbers is not complete but, in our opinion, is indicative of the situation.

5. Conclusions

We think that our data can be improved in the sense of narrowing the error range in a number of ways. We could *increase the sampling* of configurations taken in the Monte

Carlo sampling to ensure fuller convergency of our result (this however will possibly reduce our error by no more than 4 or 8%). We could *increase the number of water molecules* in the cluster to ensure that "surface effects" are not present; however, the increase must be rather large since, to be significant, the entire cluster must increase by at least one more layer, i.e., we would have to pass from 200 molecules of water to 300 with a considerable increase of computational time. This improvement, however, could resolve the problem of the determination of the second radius and coordination number for K^+ and decrease again the error by a few percent. We think that the study of the influence of one ion solvation shell on a second ion solvation shell is premature, at least until the above improvement is introduced.

The numerical technique used in this work is, however, probably the most direct technique to obtain reliable coordination numbers, in particular if one is not interested in the influence of a second ion; then a cluster with 200 molecules of water is certainly sufficiently large to accurately predict the coordination number and solvation radii for a single ion in a cluster of water. Work is in progress in this direction [18].

Acknowledgement. We wish to thank Dr. A. Martellani of the Istituto "G. Donegani" for the assistance provided during the computational stage of this work.

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Received February 16, 1976/June 1, 1976