A Molecular Dynamics Study of the Structure of an Aqueous CsF Solution

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

A molecular dynamics simulation of a 2.2 molal aqueous CsF solution has been performed employing the ST2 water model. The basic periodic cube with a sidelength of 18.50 Å contained 200 water molecules, and 8 ions of each kind, corresponding to an experimental density of 1.26 g/cm³. The simulation extended over 6.5 ps with an average temperature of 307 K. The structure of the solution is discussed by means of radial distribution functions and the orientation of the water molecules. The computed hydration numbers in the first shell of Cs^+ and F^- are 7.9 and 6.8, respectively; the corresponding first hydration shell radii are 3.22 Å and 2.64 Å, respectively. Values for the hydration shell energies and the heat of solution have been calculated.

I. Introduction

During the last decade in a series of papers from this laboratory results of Molecular Dynamics (MD) simulations of various aqueous electrolyte solutions have been reported [1 – 6]. In order to check the pair potentials employed in the simulations new x-ray measurements have been performed for most of the solutions investigated and good agreement has been found for the structural properties [7 – 10]. The information from experiments on dynamical properties of these solutions is less detailed. As far as experimental results are available in the literature, they are also in fair agreement with the results calculated from the simulations.

In the case of non simple liquids like aqueous electrolyte solutions the two main contributions from computer simulations are the predictions of properties which are not or not directly accessible by experiments and the explanation of measured macroscopical quantities on a molecular level. Of course, the predictions and explanations on the basis of the pair potentials employed in the simulations are the more reliable the better the agreement is with the available experimental data.

The information on the structure of aqueous CsF solutions available from experiments is very scarce [11]. No neutron diffraction study has been performed and only one x-ray investigation at high CsF concentrations is reported in the literature [12]. From this investigation no information on the hydration shell of F^- could be deduced as the x-ray scattering intensity of F^- is very similar to that of water.

Ab initio calculations of $F^-(H_2O)_n$ complexes have been reported by Clementi and coworkers [13, 14]. With ion-water pair potentials based on these calculations Monte Carlo (MC) simulations with one F^- surrounded by 200 water molecules have been performed and structural information has been deduced [15, 16]. MD studies of ion-water microclusters with Cs^+ and F^- from Briant and Burton [17] could not give reliable information on hydration shell structures in solution because of the small number of water molecules involved. A preliminary MD simulation of a 2.2 molal CsF solution reported by us some time ago [1] did not lead to reliable results for the F^--water interactions as the Lennard-Jones (LJ) parameters employed for F^- proved to be unsatisfactory.

The lack of experimental data on the structure of CsF solutions requires special care in the choice of the pair potentials used for the simulation in order to achieve reliable results. Therefore, in the next section the most important ion-water pair potentials chosen or proposed for the simulation of this solution so far are discussed in some detail.

In the MD study reported here, the ST2 model for water is employed again [18] and the ions are described as LJ spheres with an elementary charge at the center. The simulation technique is the same

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as described before [3]. The basic periodic cube contains 200 water molecules and 8 ions of each kind, equivalent to a 2.2 molal CsF solution. With an experimental density of 1.26 g/cm^3 the sidelength of the basic cube is 18.5 Å. The simulation extended over $3 \cdot 10^4$ time steps – which means a total elapsed time of 6.5 ps – at an average temperature of 307 K with an energy stability $|\Delta E/E|$ better than $2.4 \cdot 10^{-5}$.

The structure of the solution is discussed on the basis of various radial distribution functions (RDF) and the distribution of water molecule orientations in the hydration shells of the ions as well as around a central water molecule. Average potential energies of the water molecules as a function of distance from the ions, pair interaction energy distributions and hydration shell energies have been calculated for the subsystems. Results on dynamical properties of the CsF solution will be reported in a separate paper.

II. Effective Pair Potentials

In our previous simulations of alkali halide solutions with the ST2 model for water [18] the ions are described by LJ spheres with an elementary charge at the center [1, 2, 5]. The LJ parameters for cation-cation interactions are taken from the isoelectronic noble gases [19], the ones for anion-anion interactions are calculated from the noble gas values with the help of Pauling radii as described in detail in a previous paper [2]. Cation-anion and ion-water LJ parameters were determined by using the combination rules of Kong [20].

This choice of the LJ parameters has led to immediate agreement between the ion-water first neighbor distances from the simulation and those obtained from diffraction studies in the limits of error for all solutions investigated, without any adjustment [2, 8]. Of course, it can not be concluded that these parameter sets lead necessarily to good agreement with experimental results if a water model different from the ST2 is employed in the simulations. In addition, the agreement found for the ion-water first neighbor distances does not prove that the cation-cation and anion-anion interactions are well described by the parameter sets used. In the aqueous alkali halide solutions the like ions do not approach to a distance where the LJ parameters are relevant. It can be shown easily that beyond a separation of about 4 Å the interactions between ions are governed solely by the Coulomb law. The cation-anion LJ parameters could become relevant in solutions where contact ion pairs exist.

On the basis of this discussion it seemed justified to continue the investigation of the alkali halide solutions with the ST2 model for water and the LJ parameters from the noble gases which had proved to be successful in previous simulations. The LJ parameters employed in the MD simulation of the 2.2 molal CsF solution are given in Table 1. Recently, Fischer and Brickmann [21] calculated a set of LJ parameters for the alkali (except Cs$^+$) and the halide ions from crystal data. The F$^-$-water pair potential proposed by these authors will be compared below with the one used in this work; (the simulation of a LiCl solution by Okada et al. [22] showed that even at high concentrations crystal data do not lead necessarily to a good description of ion-ion and ion-water interactions in solution. They had to change the parameters – originally taken from crystal data – in the repulsive term of the pair potentials in order to achieve agreement with results from x-ray measurements).

The Cs$^+$-water pair potential resulting from the ST2 model for water and the LJ parameters given in Table 1 is shown in Fig. 1 for two orientations of the water molecule relative to the ion (trigonal and lone pair orbital). Not the original pair potential is drawn, but the one modified in such a way that force and potential become zero at the cut-off distance (shifted force potential) and which is really used in the simulation [3]. Ab initio calculations for Cs$^+$-water interactions have not been performed yet. LJ parameters from crystal data are not available either [21]. The pair potential employed in the MD simulation of Cs$^+$-water microclusters [17] is shown (trigonal orientation) additionally for comparison.

Table 1. (6; 12) Lennard-Jones parameters used in the simulation of the aqueous CsF solution. σ is given in Å (first row) and ε in units of 10^{-16} erg.

	Cs$^+$	F$^-$	H_2O
Cs$^+$	3.92 354.00	4.08 44.70	3.61 110.00
F$^-$		4.00 8.20	3.52 20.50
H_2O			3.10 52.61

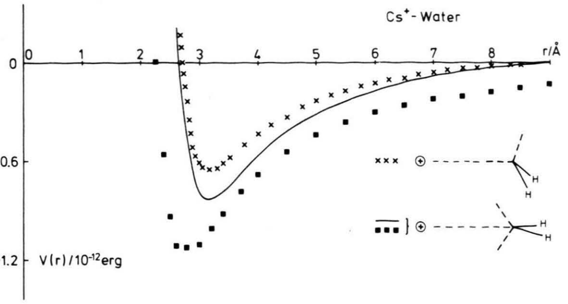

Fig. 1. Effective pair potential (shifted force potential) of the Cs^+-water interaction for the trigonal (full line) and the lone pair orbital (crosses) orientation of the water molecule. The squares give the potential (trigonal orientation) used in [17].

In Fig. 2 the Cs^+-water pair potential is given for a fixed Cs^+-O distance of 3.15 Å (the position of the energy minimum for the trigonal orientation) as a function of the angle α, which is defined in the insertion. The curve is rather flat around the trigonal orientation, where it is about 20% lower than in the lone pair orbital direction, as can also be seen from Figure 1. The simulations with ST2 water display a preference for the lone pair orbital orientation of the water molecules in the first hydration shells of all alkali ions investigated, although the ion-water pair potentials have their lowest minimum for the trigonal orientation. Only in the case of Li^+ the preferential lone pair orbital orientation is already indicated by the Li^+-water pair potential.

The same Cs^+-water pair potential has been used in a preliminary simulation [1] and has led to good agreement with x-ray diffraction studies as far as the Cs^+-water first neighbor distance is concerned. The pair potential employed by Briant and Burton (Fig. 1) has led to a wrong distance [17]. It should be mentioned that it is a general experience in our simulation of aqueous electrolyte solutions that the positions of the maxima in the ion-oxygen RDFs nearly coincide with the minima of the respective ion-water pair potentials.

The F^--water pair potential resulting from the parameters given in Table 1, is drawn for two different water molecule orientations as dashed lines in Figure 3. The pair potential really used in the simulation is the shifted force one [3] (full lines). The dots are taken from ab initio calculations of Clementi and coworkers [13]. The crosses mark the

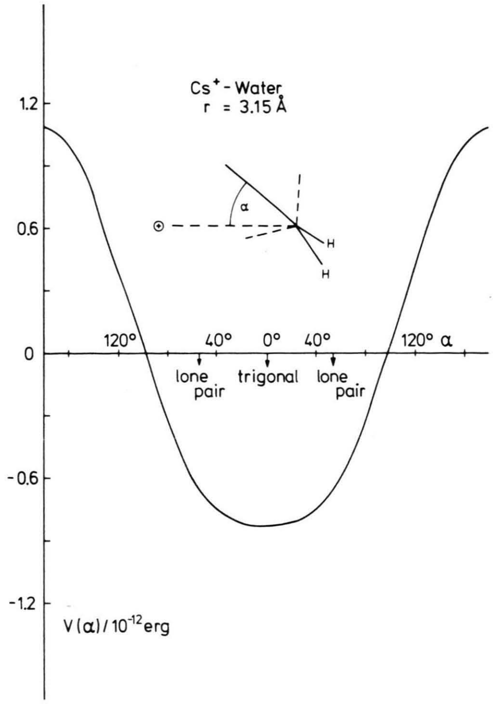

Fig. 2. The Cs^+-water pair potential at a fixed distance of 3.15 Å (energy minimum for trigonal orientation) as a function of the angle α, defined in the insertion.

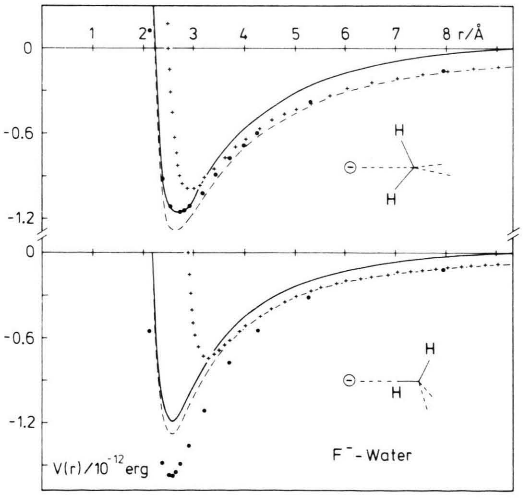

Fig. 3. The F^--water pair potentials for two different orientations of the water molecule as shown in the insertions. The dashed lines result from the ST2 model for water [18] and the LJ parameters given in Table 1, while the full lines are the corresponding shifted force potentials [3] really used in the simulation. The dots are from ab initio calculations [13] and the crosses are potentials where the LJ parameters are based on crystal data [21].

pair potentials proposed by Fischer and Brickmann where the ion-ion LJ parameters are calculated from crystal data and the Lorentz-Berthelot combination rules are employed [21]. In Fig. 4 the F^--water pair potential is shown for a fixed distance as a function of the angle Θ, defined in the insertion. The distances chosen are the distances where each pair potential has its minimum for the orientation where the dipole moment of the water molecule is directed towards F^-.

The ion-water pair potentials most appropriate for the simulation of aqueous electrolyte solutions are not necessarily the ones derived from ab initio calculations, as many body interactions have to be incorporated somehow (effective pair potentials). But one should expect that the effective pair potentials employed in the simulation reproduce significant features of the ab initio potentials like e.g. the positions of the energy minima or energetically favorable orientations. It can be seen from Figs. 3 and 4 that in this sense agreement exist between the ab initio F^--water pair potentials [13] and the ones calculated from the ST2 model for water together with the noble gas LJ parameters. A further indication for the usefulness of the F^--water pair potential as employed here results from the fact that the Cl^--water and I^--water ones calculated in the same way have led to good agreement with x-ray and neutron diffraction data [2, 5, 8].

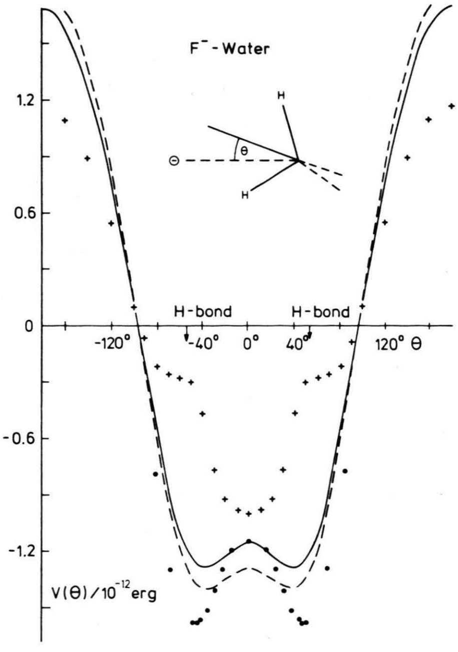

Fig. 4. The F^--water pair potentials at fixed distances as a function of the angle Θ, defined in the insertion. The positions where the pair potentials have their minima – for an orientation where the dipole moment of the water molecule is directed towards F^- – are chosen as fixed distances. The notations are the same as in Figure 3.

The F^--water pair potential proposed by Fischer and Brickmann [21] has a decisive disadvantage in so far as the potential minima for the two different water molecule orientations differ by about 0.4 Å (Fig. 3), which in turn leads to the strange angular dependence of the pair potential as shown in Figure 4. It is obvious that the quality of an ion-water pair potential can not be judged by looking at one water molecule orientation only. The strange angular dependence of the pair potential proposed in Ref. [21] has not necessarily to be attributed to the LJ parameters derived from crystal data. It might just as well be caused by the limitations of the water model employed. But even if the LJ parameters from crystal data are combined with the ST2 model the positions of the minima in the resulting ion-water pair potentials differ from ours by a few tenth of an Å. According to our experience mentioned above, this difference will lead to disagreement of the ion-water first neighbor distances with x-ray and neutron diffraction results outside the limits of experimental error.

The CsF solution is the only alkali halide solution in which even at moderate concentrations contact ion pair formation can not be excluded by experiments. Unfortunately there exists no possibility to check the LJ parameters used for the cation-anion pair potential. Therefore we have to trust that the parameters given in Table 1 lead to a correct description of this phenomenon, too.

III. Results and Discussion

A) Radial Distribution Functions

The ion-oxygen and ion-hydrogen RDFs are shown for Cs^+ and F^- in Fig. 5 together with the corresponding running integration numbers, defined by:

$$n_{xy}(r) = 4\pi\, \varrho_0 \int_0^r g_{xy}(r')\, r'^2 \mathrm{d}r' ,$$

where ϱ_0 is the number density of the water molecules. Some characteristic values of these RDFs are given in Table 2.

Table 2. Characteristic values of the radial distribution functions $g_{xy}(r)$ for the 2.2 molal CsF solution and pure water (s and p denote solvent and pure water, respectively). R_i, r_{Mi} and r_{mi} give the distances in Å where, for the i-th time, $g_{xy}(r)$ is unity, has a maximum and minimum, respectively. The uncertainties in all distances are smaller than ± 0.02 Å if not stated otherwise, and in the g values they are smaller than 3%.

xy	R_1	r_{M1}	$g_{xy}(r_{M1})$	R_2	r_{m1}	$g_{xy}(r_{m1})$	r_{M2}	$g_{xy}(r_{M2})$	$n(r_{m1})$
CsO	3.00	3.22 (4)	3.50	3.65	3.9 (2)	0.71	5.3 (3)	1.22	7.9 (8)
CsH	3.36	3.72 (4)	2.20	4.36	4.5 (2)	0.92	6.0 (2)	1.20	23 (4)
FO	2.46	2.64	7.4	2.98	3.36 (6)	0.18	4.6 (2)	1.42	6.8 (2)
FH	1.47	1.65	8.2	2.04	2.48 (8)	0.16	3.06 (4)	2.20	6.7 (1)
OO s	2.62	2.84	2.88	3.22	3.50 (4)	0.81	4.70 (5)	1.04	5.3 (2)
p	2.63	2.84	3.10	3.16	3.4 (1)	0.69	4.7 (2)	1.12	5.0 (3)
OH s	1.86	1.92	1.10	2.02	2.42 (6)	0.48	3.28 (4)	1.50	1.9 (1)
p	1.80	1.92	1.30	2.04	2.50 (4)	0.34	3.32 (4)	1.57	2.1 (1)
HH s	2.19	2.42	1.40	2.74	3.0 (1)	0.88	3.68 (8)	1.07	11.4 (9)
p	2.21	2.42	1.46	2.71	3.02 (6)	0.78	3.9 (1)	1.14	11.5 (7)

The first hydration shell of Cs^+ is not well defined as can be seen from $g_{CsO}(r)$ and $g_{CsH}(r)$ in Fig. 5, however, it is significantly more pronounced than the one of the slightly larger isoelectronic iodide ion [5]. The position of the first maximum in the Cs^+-O RDF (r_{M1}) nearly coincides with the minimum of the Cs^+-water pair potential (Fig. 1), a result which has also been found in all of our previous MD simulations of aqueous electrolyte solutions. In accordance with this finding the Cs^+-O nearest neighbor distance resulting from the MD simulation of Cs^+-water microclusters [17] is significantly smaller than our result (Figure 1). In Table 3 the Cs^+-O first neighbor distances and the hydration numbers derived from x-ray and neutron diffraction studies as well as computer simulations are compiled for comparison. The new simulation has led to a slightly larger value for r_{M1} than found in a preliminary one reported previously [1] although the same LJ parameters have been employed. The reason for this difference is the use of the shifted force potential here, which results in a small shift of the pair potential minimum. The comparison of the Cs^+-water nearest neighbor distances from diffraction measurements and from the new simulation shows that the data from the simulation lie in the upper range of the experimental values. A similar good agreement exists for the hydration numbers if one keeps in mind that the hydration numbers derived from x-ray measurements are not too reliable. The agreement found in spite of different counterions and concentrations allows the conclusion that the further predictions on the structure of the hydration shell of Cs^+ drawn from the simulation can be expected to be rather reliable.

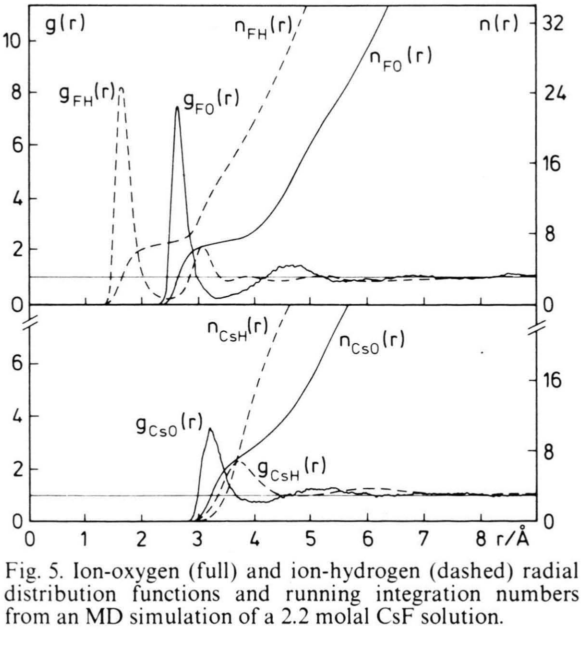

Fig. 5. Ion-oxygen (full) and ion-hydrogen (dashed) radial distribution functions and running integration numbers from an MD simulation of a 2.2 molal CsF solution.

The $g_{FO}(r)$ and $g_{FH}(r)$ together with $n_{FO}(r)$ and $n_{FH}(r)$ shown in Fig. 5 indicate a well pronounced first hydration shell around F^-. The distance of about 1 Å between r_{M1} from $g_{FO}(r)$ and $g_{FH}(r)$ points to linear hydrogen bond formation between F^- and water. The details of the orientations of the water molecules around F^- and Cs^+ are discussed below. There is no reliable information on the F^--water first neighbor distance and on the hydra-

Table 3. Comparison of the ion-oxygen first neighbor distances (I–O) and hydration numbers (n) of Cs^+ and F^- for various solutes and concentrations c [mole/l H_2O] from x-ray and neutron diffraction studies and computer simulations. The values in parenthesis result from simplified model assumptions.

Ion	Solute	c	I–O [Å]	n	Method	Ref.
Cs^+	CsF	7 – 24	3.13 ± 0.03	–	X	[12]
	CsCl CsBr CsI	2.5 – 10	3.02 – 3.22	2 – 6.2	X	[23]
	CsCl	2, 4	3.15	6	X	[24]
	CsCl	1	2.95 ± 0.10	8	N	[25]
	$Cs^+(H_2O)_{29}$	–	~ 2.9	7	MD	[17]
	CsF CsCl	2.2	3.10 ± 0.06	7.3 8.2	MD	[1]
	CsF	2.2	3.22 ± 0.04	7.9	MD	this work
F^-	NH_4F	15	(2.87)	(4)	X	[26]
	KF NH_4F	2.3 – 5.1	–	4.5	X	[27]
	$F^-(H_2O)_{200}$	–	~ 2.65	5	MC	[15]
	$F^-(H_2O)_{215}$	–	2.60	4.1	MC	[16]
	CsF	2.2	2.64 ± 0.02	6.8	MD	this work

tion number from x-ray diffraction studies as the scattering intensity and the size of F^- and water are very similar. Furthermore, neutron diffraction studies have not been reported and therefore the quality of the pair potential employed in the simulation can not be checked. Two MC calculations are available for comparison (Table 3). There exists agreement in r_{MI} between MC and MD simulations although pair potentials from rather different sources have been used. The hydration numbers from MC are smaller than from MD which might be a consequence of the different water models employed. As an experimental check of the pair potentials is needed, new x-ray measurements of a 2.2 molal CsF solution are in preparation at the Central Research Institute for Chemistry of the Hungarian Academy of Sciences in Budapest.

In Fig. 6 the intermolecular $g_{\mathrm{OO}}(r)$, $g_{\mathrm{OH}}(r)$, and $g_{\mathrm{HH}}(r)$ and the corresponding running integration numbers $n(r)$ for the water molecules in the 2.2 molal CsF solution are compared with the ones from a simulation of pure ST2 water. Characteristic data of these RDFs are given in Table 2.

The height of the first peak of $g_{\mathrm{OO}}(r)$ in the CsF solution is lower and the first minimum less pronounced than in pure water, as in all alkali halide (except LiI) solutions investigated so far [5]. The number of nearest neighbor water molecules around a central one is, in the limits of error, the same in the solution and in pure water. The reason for the different behavior of the LiI solution is the octahedral arrangement of the six water molecules in the first hydration shell of the small Li^+, leading to an O–O distance very near 3 Å, the range of the first peak in $g_{\mathrm{OO}}(r)$. The enhancement of these

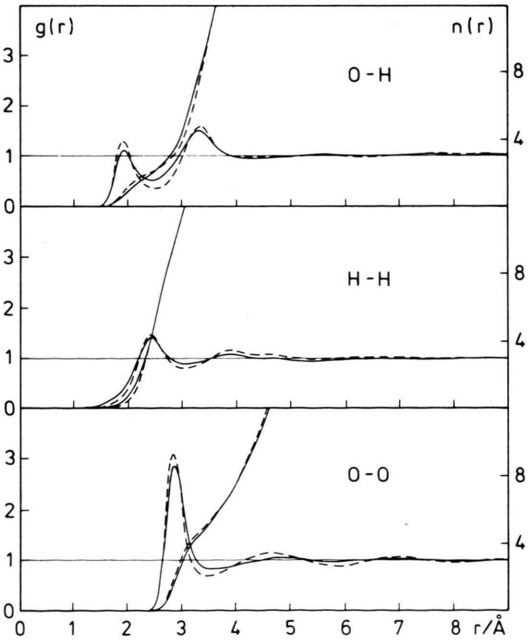

Fig. 6. Oxygen-oxygen, oxygen-hydrogen and hydrogen-hydrogen intermolecular radial distribution functions and running integration numbers for the water molecules from an MD simulation of a 2.2 molal CsF solution (full) and pure water (dashed).

O–O distances exceeds the reduction caused by the excluded volume effect of the Li^+ and results consequently in a larger number of first neighbor water molecules in the LiI solution compared with pure water. Similar results have been found for a $MgCl_2$ solution [6]. The larger cation in the CsF solution does not show this enhancement and only the excluded volume effect remains.

The changes in $g_{OH}(r)$ and $g_{HH}(r)$ caused by the ions are again smaller in the case of the CsF solutions than in solutions with small cations. The strongly favored lone pair orbital orientation of the water molecules in the first hydration shell of Li^+ [5] and Mg^{++} [6] reduces the possibilities for hydrogen bond formation and results in a decrease of the first peak in $g_{OH}(r)$. The influence of the large Cs^+ on the orientation of the water molecules is less strong and therefore the change of $g_{OH}(r)$ is smaller when compared with pure water. A similar excluded volume effect of the anion on $g_{HH}(r)$ is much less significant because of the formation of linear hydrogen bonds leaving the lone pair orbitals of the hydration shell water molecules free for hydrogen bonds with neighboring water molecules.

The ion-ion RDFs are shown in Fig. 7 together with the running integration numbers. The curves are drawn from a histogram with an increment of 0.02 Å. The strong noise results from the small number of ions in the basic cube. The same increment has been used for the other RDFs in Figs. 5 and 6 thus allowing a judgement on the relative statistical uncertainty. The $g_{CsCs}(r)$ and $g_{FF}(r)$ seem to have no significant structure outside of statistical noise. They indicate that the nearest distance of approach of two like ions is the one, where the two ions are separated by just one water molecule.

The Cs^+-F^- RDF is of special interest as the CsF solution was the only alkali halide solution investigated by us so far, where the simulation indicated a possible formation of contact ion pairs [1]. But even this simulation, which extended over 6.5 ps, does not give a definite answer. It is interesting to note that the smallest Cs^+-F^- distance was 6.5 Å when the simulation started. Then a Cs^+ and a F^- approached forming a contact ion pair after about 6 ps and remained together for the rest of the simulation time. The small bump in $g_{CsF}(r)$ at about 3.5 Å indicates this. If they would stick together for a longer period of time and no additional contact ion pair would be formed, one would have to conclude (as before [1]) that about one out of ten ions are paired. There seems to be a peak in $g_{CsF}(r)$ between 5–6 Å outside of statistical noise indicating the existence of Cs^+ and F^- which are separated by just one water molecule. Similar configurations of unlike ions have been found in the simulation of a LiI solution, too [5].

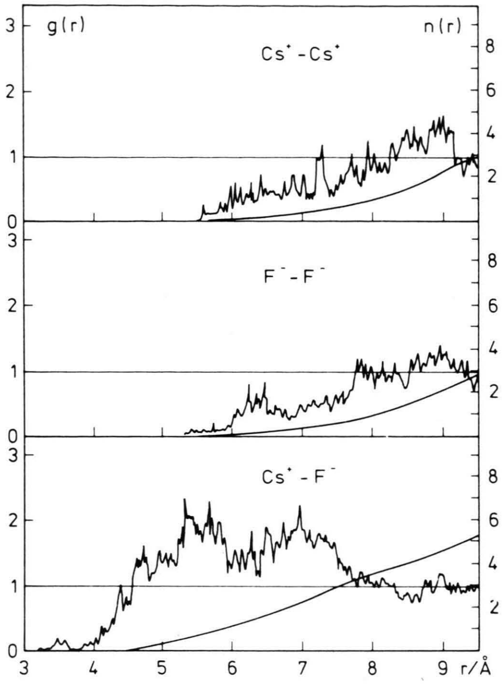

Fig. 7. Ion-ion radial distribution functions and running integration numbers for a 2.2 molal CsF solution.

B) Orientation of the Water Molecules

It has been discussed recently [10] that the information on the orientation of the water molecules in the first hydration shells of the ions, which can be deduced from the distance of the first peaks in the ion-oxygen and ion-hydrogen RDFs, is only of limited significance even if the hydration shells are well pronounced as in the case of Mg^{++}. Therefore, the average value of $\cos\Theta$ has been calculated directly from the simulation as a function of the ion-oxygen distance and is shown for Cs^+ and F^- in Figure 8. $\Theta = 180° - \alpha$ is defined as the angle between the dipole moment direction of the water molecule and the vector pointing from the oxygen atom towards the center of the ion.

In the case of Cs^+ $\langle \cos \Theta(r) \rangle$ increases strongly from -0.64 to -0.25 over the range of the first peak in $g_{CsO}(r)$. The distribution of $\cos \Theta$ for the eight water molecules in the first hydration shell, shown in Fig. 9, is very broad (as expected from Fig. 8), but preference for a lone pair orbital orientation is obvious. From the Cs^+-water pair potential (Fig. 2) a slight preference for a trigonal orientation could be expected. But the additional interactions with the neighboring water molecules make the lone pair orbital orientation energetically more favorable.

It should be mentioned that a discrepancy exists in respect to the orientation of the water molecules in the first hydration shells of the cations. The MD simulations with the ST2 model for water indicate a preference of the lone pair orbital orientation not only for Cs^+, but also for Li^+ [5] and Na^+ [1]. The neutron diffraction studies lead for Cs^+ [25] and for Li^+ [28] to the same conclusion. The MD simulations with the Central Force model for water indicate for Na^+ [4] and Mg^{++} [6] a preference for trigonal orientation as well as the MC studies of Li^+, Na^+ and K^+, where pair potentials based on ab initio calculations are employed (Fig. 8 of [16]). Obviously the orientation deduced from the simulation depends upon the water model used. The negative charges in the ST2 model might exaggerate the directionality of the lone pair orbitals.

All simulations agree with experimental indications on a preference for a linear hydrogen bond formation between the halide ions and the water molecules in their first hydration shells. This orientation is strongly preferred for F^- as can be seen from Figures 8 and 9. The $\langle \cos \Theta(r) \rangle$ is constant over the whole range of the first peak in $g_{FO}(r)$ with a value of 0.6, equivalent to half of a tetrahedral angle (Figure 8). This angle is not only the mean value for the orientation of the water molecules in the first hydration shell of F^-, but also the by far most probable one as can be seen from the narrow distribution in Figure 9.

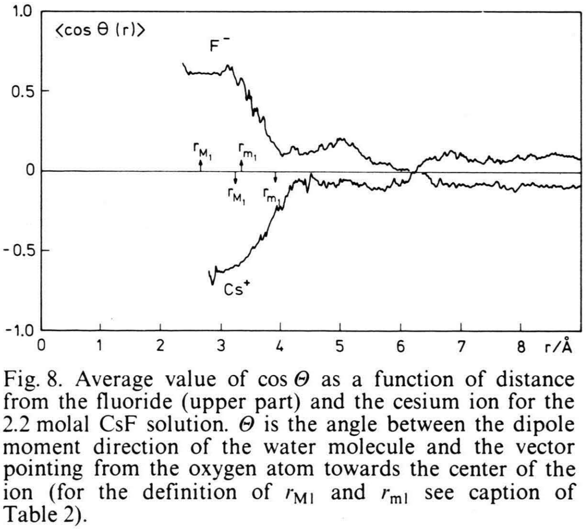

Fig. 8. Average value of $\cos \Theta$ as a function of distance from the fluoride (upper part) and the cesium ion for the 2.2 molal CsF solution. Θ is the angle between the dipole moment direction of the water molecule and the vector pointing from the oxygen atom towards the center of the ion (for the definition of r_{MI} and r_{mI} see caption of Table 2).

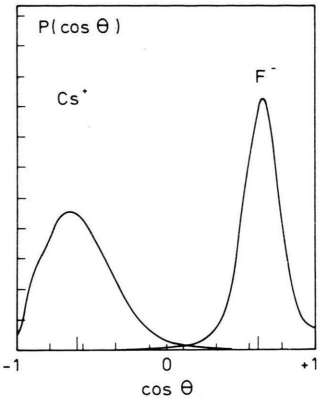

Fig. 9. Distribution of $\cos \Theta$ in the first hydration shells of Cs^+ and F^- for a 2.2 molal CsF solution. The marks indicate the mean value of $\cos \Theta$. The definition of Θ is given in the caption of Figure 8. The distributions are normalized and given in arbitrary units.

The influence of both ions on the orientation of the water molecules decreases rapidly after a distance of about 3 Å (Figure 8). This feature has been found, independent of the size of the ions, in all our simulations of alkali halide solutions where the ions are described as LJ spheres with an elementary charge at the center. Beyond a distance of about 4.5 Å a significant preferential orientation exists only in the case of the small ions where the influence of the ions extends further through the strongly oriented water molecules in the first hydration shell, leading also to the formation of a second hydration shell. The change of sign of $\cos \Theta(r)$ at about 6.5 Å (Fig. 8) might be caused by the shifted force potential which reduces the ion-water forces to zero at the cut-off distance thus allowing the neighboring water molecules and other ions to govern the orientation.

The average value of $\cos \Theta_{ww}$, where Θ_{ww} is the angle between the dipole moment directions of two water molecules, is given in Fig. 10 as a function of

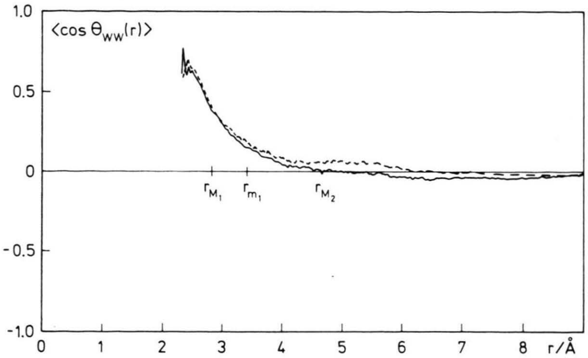

Fig. 10. Average value of the cosine of the angle Θ_{ww} between the dipole moment vectors of two water molecules in the 2.2 molal CsF solution (full) and in pure ST2 water (dashed) as a function of the distance between the two oxygen atoms.

the O–O distance for the water molecules in the 2.2 molal CsF solution and for pure ST2 water (dashed). The distribution of $\cos \Theta_{ww}$ for the nearest neighbor water molecules around a central one for O–O distances up to 3.5 Å is shown in Figure 11. It can be seen from both figures that Cs$^+$ and F$^-$ do not disturb the relative orientations of the water molecules significantly. This is different from what has been found for the LiI solution [5], where especially in the short distance range the relative orientations of the water molecules in the solution differ from that in pure water. Obviously this is caused by strongly oriented water molecules in the first hydration of Li$^+$ and the existence of a second shell.

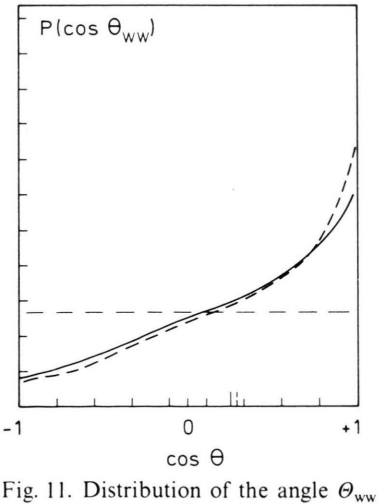

Fig. 11. Distribution of the angle Θ_{ww} between the dipole moment vectors of two water molecules in the 2.2 molal CsF solution (full) and in pure ST2 water (dashed) for nearest neighbor water molecules with O–O distances up to 3.5 Å. The average values of $\cos \Theta_{ww}$ are marked on the abscissa.

C) Average Potential Energies and Pair Interaction Energy Distributions

The average potential energies of a water molecule in the field of a cesium and a fluoride ion are shown in Fig. 12 as a function of the ion-oxygen distance. For comparison the effective ion-water pair potentials are drawn for the most favorable orientations – trigonal for Cs$^+$ (Fig. 1) and linear hydrogen bond formation for F$^-$ (Fig. 3). Up to the potential minima or maxima of the ion-oxygen RDFs (equivalent statements, see above) the water molecules assume the energetically most favorable orientation. With increasing distance the influence of the central ion decreases and the orientation of the water molecules is more and more determined by neighboring water molecules and other ions. At ion-oxygen distances above about 4 Å the difference between $V_{\mathrm{IonW}}(r)$ and the effective pair potential shown becomes even independent of the ion size. $\langle V_{\mathrm{FW}}(r) \rangle$ is different from a previously reported one [1] as improved LJ parameters [2] are employed in this simulation.

The ion-water potential energy distributions in Fig. 13 reflect the more or less pronounced first hydration shells of F$^-$ and Cs$^+$, respectively, with relative maxima at -1.18 for F$^-$ and $-0.69 \cdot 10^{-12}$ erg for Cs$^+$. Different from $P(V_{\mathrm{LiW}})$ [5] the larger F$^-$ shows no indication of a second hydration shell and also no shoulder at the positive energy side, which has been explained as the competing influence of

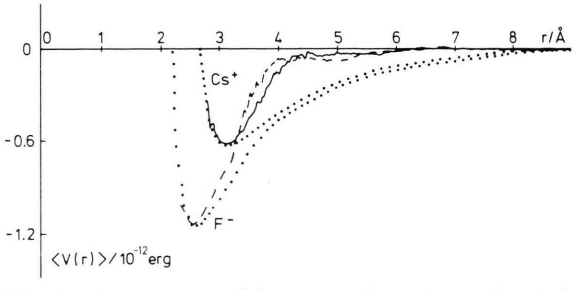

Fig. 12. Average potential energy of a water molecule in the field of a cesium ion (full) and a fluoride ion (dashed) as a function of the ion-oxygen distance in a 2.2 molal CsF solution. The dots indicate the effective ion-water pair potentials for trigonal orientation in the case of Cs$^+$ and a linear hydrogen bond formation in the case of F$^-$.

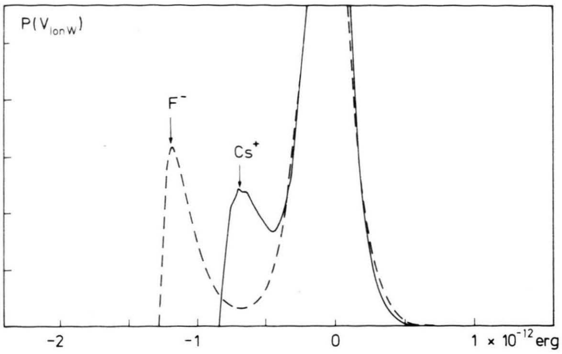

Fig. 13. Pair interaction energy distribution for Cs^+-water (full) and F^--water (dashed) in a 2.2 molal CsF solution. $P(V_{\mathrm{Ion W}})$ is given in arbitrary units.

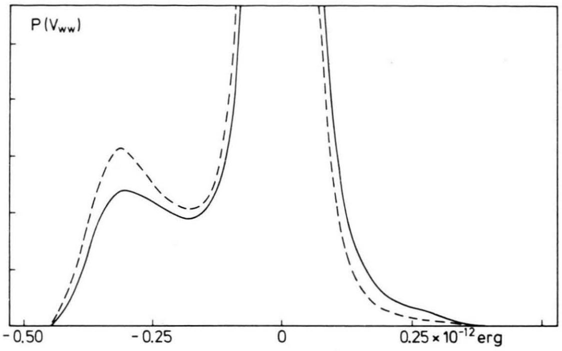

Fig. 14. Pair interaction energy distribution for water-water in a 2.2 molal CsF solution (full) and in pure ST2 water (dashed). $P(V_{\mathrm{ww}})$ is given in arbitrary units.

two Li^+ on the orientation of the two molecules in between them.

The water-water pair interaction energy distribution in the 2.2 molal CsF solution is compared in Fig. 14 with the one for pure ST2 water. The characteristic changes are the lowering of the height of the relative maximum (positioned at $-0.29 \cdot 10^{-12}$ erg) and minimum at the negative energy side and a significant increase in the number of water molecules with a positive pair interaction energy. This influence of the ions on the energy distribution is different from what has been found from a simulation of pure water at higher temperatures [18]. An increase in temperature leads also to a lowering of the height of the relative maximum but the minimum is filled up simultaneously, keeping in this way the number of water molecules with negative pair interaction energy nearly constant. The influence of the ions on the structure of water consists not only of hydrogen bond breaking as an increase in temperature does but, in addition, the ions force the water molecules into orientations relative to each other so unfavorable that positive energies result.

D) Heat of Solution

The integrated energies of hydration, defined by:

$$V_\alpha^{\mathrm{h}}(r) = 4\pi\,\varrho_0 \int_0^r g_{\alpha \mathrm{O}}(r')\,\langle V_{\alpha \mathrm{w}}(r')\rangle\, r'^2\,\mathrm{d}r'$$

are shown in Fig. 15 as a function of r. The difference in $V_{\mathrm{w}}^{\mathrm{h}}$ at 9 Å between pure water and the CsF solution of almost a factor of two results from the structure breaking influence of the ions as discussed above and from the excluded volume effect. The water dimer energy averaged over the first four neighbours differs significantly between solution (− 0.18) and pure water (− 0.27), while the absolute energy minimum of the ST2 water dimer is $-0.47 \cdot 10^{-12}$ erg. The decrease of $V_{\mathrm{w}}^{\mathrm{h}}(r)$ outside of the sphere of the first neighbors is more pronounced in the case of pure water than in the solution; this also indicates a strong reduction of the far reaching correlation between the solvent molecules.

In the case of the ions the large difference between the corresponding integrated energies of hydration results mainly from the different ion size.

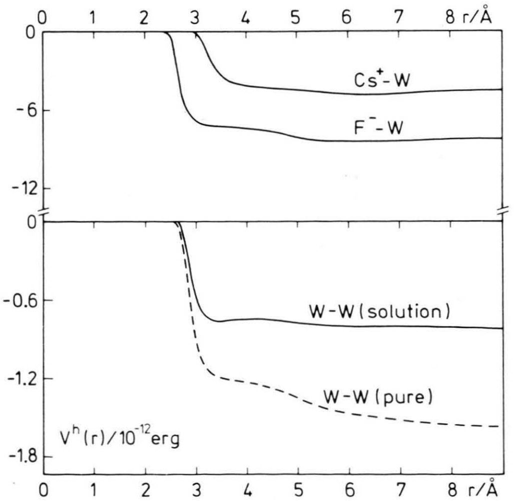

Fig. 15. Integrated energy of hydration for ion-water and water-water interactions in the 2.2 molal CsF solution (full) and in pure ST2 water (dashed) as a function of ion-oxygen and oxygen-oxygen distances.

The average potential energy of a hydration water molecule of Cs^+ (F^-) is 60% (91%) of the absolute energy minimum of the ion-water pair potential, but because of the different hydration numbers, both $V^{\text{h}}_{\text{Cs}}(r)$ and $V^{\text{h}}_{\text{F}}(r)$ reach about 86% of their asymptotic values for large r within the first hydration shells.

The calculated potential energy of the 2.2 molal CsF-solution (V^{solution}) is $-$ 414.1 kcal per mole of CsF salt. This value consists of $-$ 82.1 kcal ion-ion, $-$ 183.3 kcal ion-water and $-$ 148.7 kcal water-water contribution. As the calculated potential energy of 25 mole of pure water – which in a 2.2 molal solution are combined with one mole salt – at a temperature of $T = 307$ K (V^{water}) is $-$ 234 kcal, the molar internal energy of transfer of one mole of CsF salt into water, defined in the thermocycle of Ref. [29], is

$$\langle V^{\text{solution}} \rangle - \langle V^{\text{water}} \rangle = -\,179.6\ \text{kcal}\,.$$

The comparison of this quantity with the enthalpies of hydration of one mole of gaseous ions at $T = 298$ K [30] for Cs^+ ($-$ 75.2 kcal) and for F^- ($-$ 113.3 kcal) shows that the calculated internal energy of transfer is consistent with this value. From the lattice energy of CsF ($-$ 175.7 kcal/mole) [31], together with the calculated potential energy difference between the 2.2 molal CsF solution and pure ST2 water at $T = 307$ K a value of $-$ 3.9 kcal/mole results for the heat of solution, while the experimental value is $-$ 8.4 kcal/mole at $T = 288$ K [32]. With the ST2 water model the dissolution of the CsF salt is an exothermic process, as is observed experimentally. The difference of 4.5 kcal/mole is not surprising if it is taken into account that the heat of solution is the small difference of two big numbers, one taken from literature and the other calculated from the simulation.

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