A Molecular Dynamics Study of Aqueous Solutions
V. Angular Distribution of the Water Dipoles in the Hydration Shells of Various Alkali- and Halide Ions

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The angular distributions of the water dipoles have been calculated from molecular dynamics runs for the first hydration shells of various ions in 2.2 molal LiJ, LiCl, NaCl, CsCl and CsF solutions and in a 0.55 molal NaCl solution. It is shown how the distributions depend on the size of the shell taken around each ion. The results give no indication for the existence of desoriented water molecules in the immediate neighbourhood of the ions.

Introduction

Experimental information on the orientation of the water molecules in the first hydration shells of ions has been deduced from NMR measurements [1], dielectric investigations [2] and x-ray and neutron diffraction studies [3]. From these investigations it has been concluded that a linear hydrogen bond is formed between the water molecules and F^- as well as Cl^-. The available information on this subject from quantum mechanical calculations, leading to the same conclusion for these two ions, has been reviewed by Schuster, Jakubetz and Marius [4]. Molecular dynamics studies of aqueous alkali halide solutions show, in agreement with these results, that a lone pair orbital of the water molecules is directed towards the cations and a linear hydrogen bond is formed with the anions [5].

Besides some short remarks in a previous paper [5] the available knowledge so far concerns only the preferential orientation of the water molecules in the first hydration shells of the ions. There exists a lack of information on the angular distribution of the water dipoles. This distribution is of great interest in connection with the discussion of positive and negative hydration [6, 7] and with ion hydration studies when a distinction is made between solvation and coordination numbers [8]. In both cases the existence of desoriented water molecules in the first hydration shells of the ions is assumed.

From the molecular dynamics studies as described in detail in two previous papers [5, 9] these angular distribution functions have been calculated for the various ions in 2.2 molal LiJ, LiCl, NaCl, CsCl and CsF solutions and in a 0.55 molal NaCl solution and are reported here.

Results and Discussion

The orientation of the water molecules in the hydration shells of ions is described by Θ, the angle between the dipole moment vector of the water molecule and the vector pointing from the oxygen atom to the centre of the ion (see Figure 1). The angular distribution functions $P(\cos\Theta)$ for the various ions have been calculated for the water molecules in three different spheres around each ion in order to show how the distribution functions change when the number of water molecules included in the distribution is increased. The radii of the three spheres have been chosen to be r_{M1}, R_2 and r_{m1}, the distances for which the ion-oxygen radial distribution functions have their first maximum, are one for the second time and have their first minimum, respectively [5].

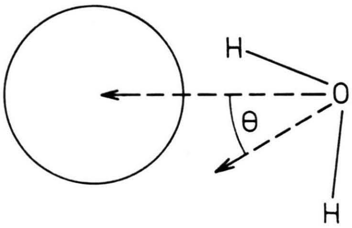

Fig. 1. Definition of the angle Θ.

$P(\cos\Theta)$ is given in Figs. 2 and 3 in form of histograms for the various ions in 2.2 molal LiJ, LiCl, CsCl and CsF solutions and in 2.2 molal and

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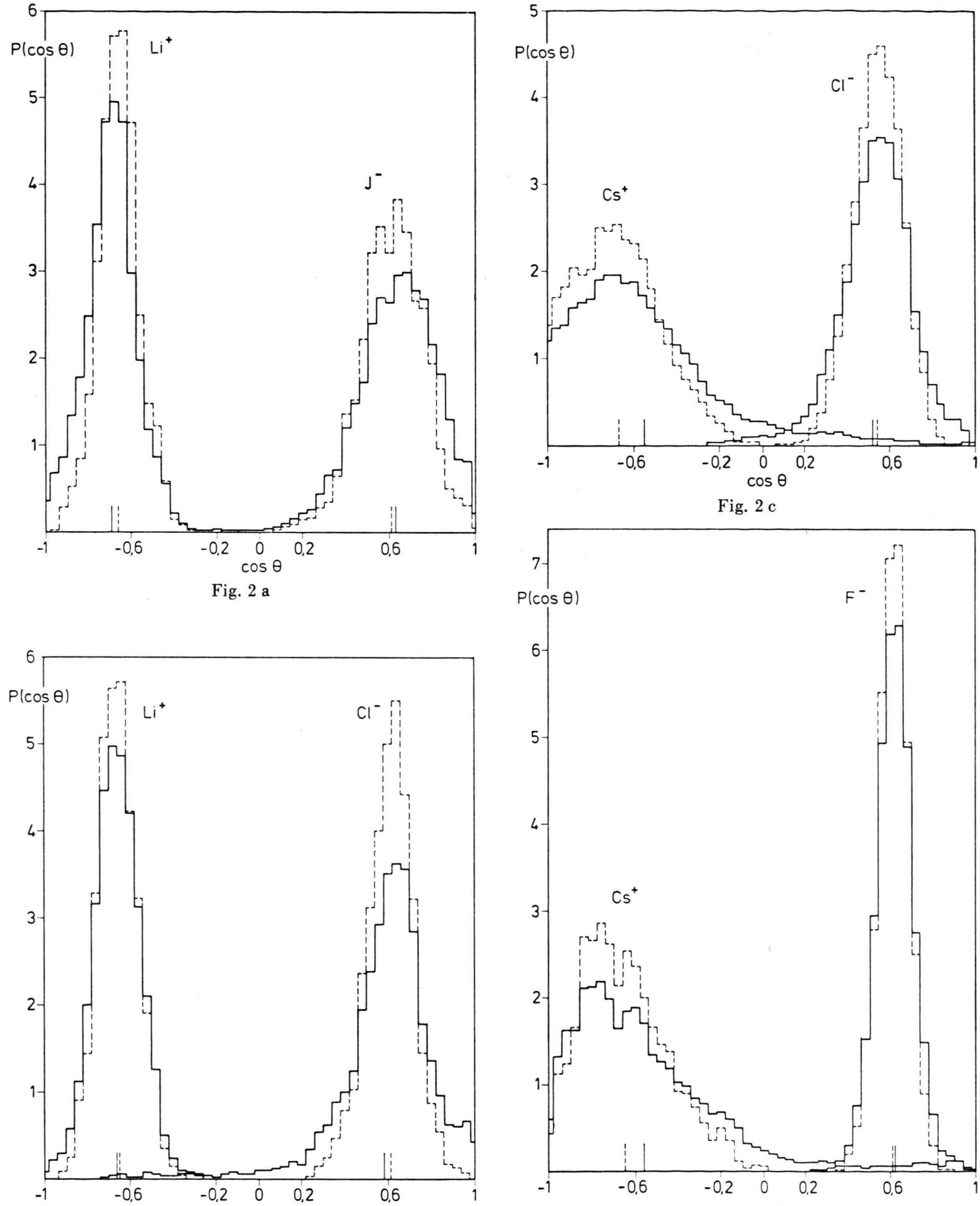

Fig. 2 a

Fig. 2 b

Fig. 2 c

Fig. 2 d

Fig. 2. Angular distribution of the water dipoles in the hydration shells of various ions in four different 2.2 molal alkali halide solutions. The dashed and full histograms give the distributions for the water molecules in two different spheres around each ion with radii r_{M1} and r_{m1} respectively. r_{M1} and r_{m1} are the distances where the ion-oxygen radial distribution functions have their first maximum and first minimum. The distributions are normalized and given in arbitrary units. The intervalls of cos Θ are 0.04. The marks on the abscissa indicate the corresponding mean values of cos Θ. a, b, c and d refer to LiJ, LiCl, CsCl and CsF solutions respectively.

0.55 molal NaCl solutions, respectively. In order to prevent overcrowding only the distribution functions corresponding to r_{M1} (dashed lines) and r_{m1} (full lines) are shown in the figures. All histograms are normalized and given in arbitrary units. The mean value for each distribution is marked on the abscissa.

The distances r_{M1}, R_2 and r_{m1}, the mean value of $\cos \Theta$ and the average deviation from these mean values being a quantitative measure of the width of the angular distribution are given in Table 1 for the various ions in the different alkali halide solutions.

It is obvious from Figs. 2 and 3 that $P(\cos \Theta)$ for both spheres narrows with decreasing ion size for cations as well as for anions as expected. Comparing cations and anions of similar size (e. g. Na^+ and F^-) it can be seen that the angular distributions are sharper in the case of the anions. This is even true when F^- is compared with Li^+. Although this general trend is not in question, a word of caution seems to be necessary at this point. As our molecular dynamics runs lead to average anion-oxygen distances in the first hydration shells which are significantly smaller when compared with x-ray diffraction studies (see Table 3 in Ref. 5), the calculated angular distribution for the anions might be too narrow.

The difference between dashed and full line histograms is most strongly pronounced in the case of Cs^+. The large positive tail completely disappears and accordingly the mean value of $\cos \Theta$ decreases significantly. This is a clear indication that there is a strong decrease in the orientation of the water molecules in the range between r_{M1} and r_{m1}. Although not shown in Fig. 2 it can be seen from corresponding values of $\langle \cos \Theta \rangle$ and $\langle (\Delta \cos \Theta)^2 \rangle$ in Table 1 that most of this effect occurs in the range between R_2 and r_{m1}.

The angular distributions for Li^+ and Cs^+ do not change significantly with an exchange of the counterions. The difference in $\langle \cos \Theta \rangle$ existing between Li^+ and Na^+ at one side and Cs^+ at the other side for r_{m1} has disappeared for r_{M1}.

For all anions the change in $\langle \cos \Theta \rangle$ is quite small when going from r_{m1} to r_{M1} because of the generally narrower distributions when compared with Cs^+. With respect to counterion dependence there is only a significant difference in $\langle \cos \Theta \rangle$ being much smaller in the CsCl solution.

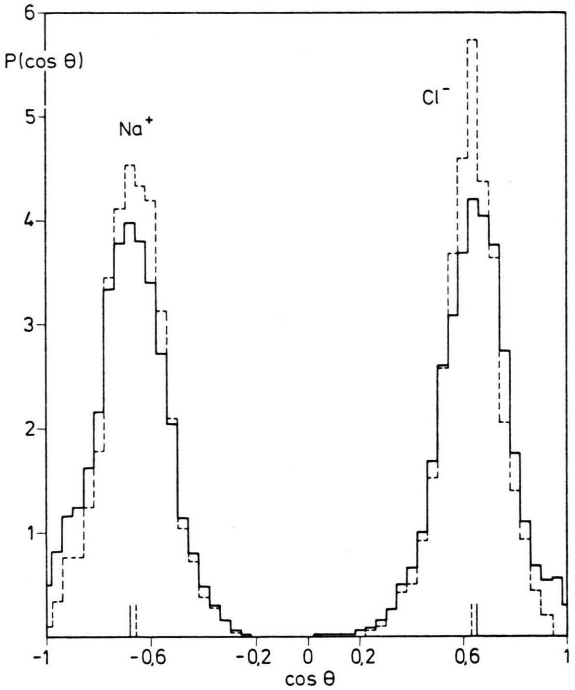

Fig. 3 a

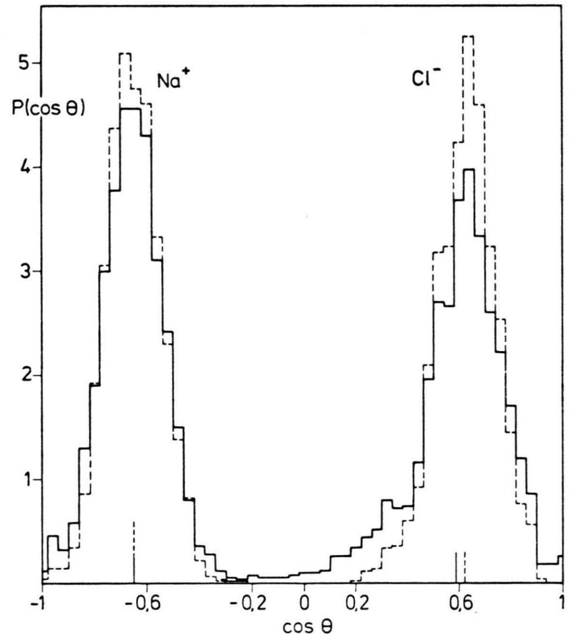

Fig. 3 b

Fig. 3. Angular distribution of the water dipoles in the hydration shells of Na^+ and Cl^- in a 2.2 molal and a 0.55 molal NaCl solution. a and b refer to the 2.2 and 0.55 molal solutions respectively. For further explanation see caption of Figure 2.

A change of concentration does not affect significantly the angular distribution around Na^+ as can be seen from Figure 3. For Cl^- the distribution is slightly broader at the lower concentration and the larger sphere.

In conclusion it can be stated that the molecular dynamics calculations give no indication for the existence of desoriented water molecules in the immediate neighbourhood of the alkali or halide ions investigated here. Therefore there remains some doubt if negative hydration can be understood on the basis of such kinds of water molecules [6, 7]. For the same reason a distinction between solvated and coordinated water molecules on the basis of water molecule orientation [8] seems to be questionable.

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Table 1. Mean values of $\cos\Theta$ and the average square deviations from these mean values for the water molecules in three different spheres around various alkali and halide ions in 2.2 molal LiJ, LiCl, NaCl (a), CsCl and CsF solutions and in 0.55 molal NaCl (b) solution. The radii of the three spheres r_{M1}, R_2 and r_{m1} are the distances where the ion-oxygen radial pair distribution functions have their first maximum, are unity for the second time and have their first minimum respectively [5].

Ion	Solute	r_{M1} Å	R_2 Å	r_{m1} Å	$\langle\cos\Theta\rangle$			$\langle(\Delta\cos\Theta)^2\rangle$		
					r_{M1}	R_2	r_{m1}	r_{M1}	R_2	r_{m1}
Li	LiJ	2.10	2.47	3.1	−0.66	−0.68	−0.69	0.009	0.013	0.016
	LiCl	2.06	2.34	2.72	−0.65	−0.66	−0.66	0.009	0.011	0.012
Na	NaCl [a]	2.31	2.57	3.11	−0.66	−0.68	−0.68	0.015	0.018	0.019
	NaCl [b]	2.32	2.63	3.10	−0.65	−0.65	−0.65	0.011	0.014	0.015
Cs	CsCl	3.10	3.50	4.14	−0.67	−0.63	−0.55	0.041	0.057	0.138
	CsF	3.10	3.45	3.9	−0.65	−0.62	−0.55	0.040	0.063	0.128
F	CsF	2.22	2.49	2.92	0.61	0.61	0.62	0.005	0.008	0.009
Cl	LiCl	2.68	3.05	3.88	0.61	0.61	0.58	0.012	0.020	0.057
	NaCl [a]	2.66	2.96	3.40	0.63	0.64	0.65	0.013	0.017	0.020
	NaCl [b]	2.68	3.03	3.53	0.62	0.61	0.59	0.014	0.024	0.037
	CsCl	2.66	3.04	3.55	0.54	0.53	0.52	0.014	0.026	0.039
J	LiJ	3.02	3.47	3.7	0.61	0.63	0.63	0.021	0.029	0.033

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