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 $\Theta$, 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 $r_{11}$, $R_2$ and $r_{11}$, 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.

$P(\cos \Theta)$ 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...
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 intervals of $\cos \theta$ are 0.04. The marks on the abscissa indicate the corresponding mean values of $\cos \theta$. 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 \( r_{ml} \) (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 \( r_{ml} \), 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. \( \text{Na}^+ \) and \( \text{F}^- \)) it can be seen that the angular distributions are sharper in the case of the anions. This is even true when \( \text{F}^- \) is compared with \( \text{Li}^+ \). 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 \( \text{Cs}^+ \). 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 \( r_{ml} \). 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 \( r_{ml} \).

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

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

Fig. 3a

Fig. 3b

Fig. 3. Angular distribution of the water dipoles in the hydration shells of \( \text{Na}^+ \) and \( \text{Cl}^- \) 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. For the same reason a distinction between solvated and coordinated water molecules on the basis of water molecule orientation 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 $r_{M1}$, $r_{M2}$ and $r_{M3}$ 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.

<table>
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<tr>
<th>Ion</th>
<th>Solute</th>
<th>$r_{M1}$ (Å)</th>
<th>$r_{M2}$ (Å)</th>
<th>$r_{M3}$ (Å)</th>
<th>$\langle \cos \Theta \rangle$</th>
<th>$\sigma_{\cos \Theta}$</th>
<th>$\langle (\cos \Theta)^2 \rangle$</th>
<th>$\sigma_{(\cos \Theta)^2}$</th>
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<td>Li</td>
<td>LiJ</td>
<td>2.10</td>
<td>2.47</td>
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<td>-0.68</td>
<td>-0.69</td>
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<td>LiCl</td>
<td>2.06</td>
<td>2.34</td>
<td>2.72</td>
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<td>-0.66</td>
<td>-0.66</td>
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<td>Na</td>
<td>NaCl a</td>
<td>2.31</td>
<td>2.57</td>
<td>3.11</td>
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<td>-0.68</td>
<td>-0.68</td>
<td>0.015</td>
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<td>NaCl b</td>
<td>2.32</td>
<td>2.63</td>
<td>3.10</td>
<td>-0.65</td>
<td>-0.65</td>
<td>-0.65</td>
<td>0.011</td>
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<tr>
<td>Cs</td>
<td>CsCl</td>
<td>3.10</td>
<td>3.50</td>
<td>4.14</td>
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<td>-0.63</td>
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<td>CsF</td>
<td>3.10</td>
<td>3.45</td>
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<td>-0.55</td>
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<td>2.49</td>
<td>2.92</td>
<td>0.61</td>
<td>0.61</td>
<td>0.62</td>
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<td>3.05</td>
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<td>0.61</td>
<td>0.58</td>
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<td>0.63</td>
<td>0.63</td>
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