A Molecular Dynamics Study of Aqueous Solutions

I. First Results for LiCl in H_2O

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(Z. Naturforsch. **29 a**, 1164–1171 [1974]; received May 3, 1974)

First results of a molecular dynamics study of an aqueous LiCl solution are reported. The system investigated consisted of 216 particles, 198 water molecules, 9 lithium ions, and 9 chloride ions. The calculations lead to fair agreement with the static properties of the first hydration shells of the ions as derived from X-ray and neutron diffraction studies, and with kinetic properties as derived from NMR measurements. A model for the motion of the water molecules in the first hydration sphere of Li^+ is tentatively proposed.

I. Introduction

The successful attempts of Rahman and Stillinger [1–4] to study liquid water using the techniques of molecular dynamics encourage the investigation of aqueous electrolyte solutions using the same methods. Molecular dynamics calculations are expected to lead to valuable information on the influence of the ions on water, e. g. information about changes of static as well as kinetic properties.

The alkali halides with their spherically symmetrical charge distribution offer themselves as a reasonable starting point for the calculations. A LiCl solution was chosen basically for two reasons. The effects of the ion on the water molecules in the first hydration sphere are very pronounced in the case of Li^+ because of the small size of the ion. In addition there is a large body of experimental data on LiCl solutions, which offers an excellent chance to compare the results of the molecular dynamics calculations with experimental evidence. Specifically, the X-ray and neutron diffraction studies of Narten, Vaslow, and Levy [5] offer information on static properties, while the NMR investigations of Hertz, Tutsch, and Versmold [6] lead to information on the motions of the water molecules in the first hydration sphere.

In order to test the usefulness of such calculations with a minimum of computer time, a relatively small system with 216 particles is utilized. To get reasonable statistics with a limited number of time steps a ratio of ions to water molecules of 1:11 is chosen. The size of the periodic box is chosen to give the experimental density of a 2 molal LiCl solution. A switching function is introduced in the pair potentials for ion-ion and ion-water interactions at distances larger than the first hydration shell allowing the coulombic interactions to decrease smoothly to the cut-off distance.

The first results reported here for static and kinetic properties are of a more qualitative nature because of the limited statistics. In spite of this limitation there seems to be sufficient evidence to propose a tentative model of the motions of the water molecules in the first hydration sphere of Li^+.

The results of these first molecular dynamics calculations of the properties of aqueous solutions are promising and justify a continuation and expansion of the calculations.

II. Effective Pair Potentials

The total potential was developed as the sum of effective pair potentials. For the water molecule the ST2 point charge model [4] illustrated in Fig. 1 was used, while the ions were treated as point charges residing at the center of Lennard-Jones spheres.

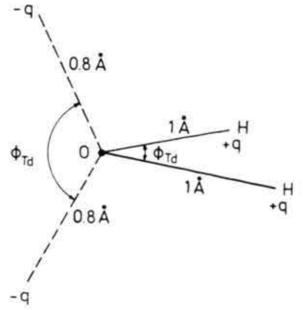

Fig. 1. The ST2 point charge model for water similar to that used in the molecular dynamics calculations by Stillinger and Rahman [4]. The tetrahedral angle $\Phi_{Td} = 109° 28'$ and $q = 0.23$ e.

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Each of the six pair potentials consists of a Lennard-Jones and a Coulomb term:

$$V_{ij}(r, d_{11}, d_{12} \ldots) = V_{ij}^{\mathrm{LJ}}(r) + V_{ij}^{\mathrm{C}}(r, d_{11}, d_{12} \ldots) \tag{1}$$

where i and j refer to Li^+, Cl^-, or water. r denotes the distance between the Lennard-Jones centers of the two particles. For an ion the Lennard-Jones center is located at the center of the mass, while for a water molecule it is located at the oxygen atom. As the pair potential is dependent on the orientation of the water molecule, the Coulombic term is calculated using $d_{\alpha\beta}$, the distances between the point charges on the two particles i and j. Since the orientation of the water molecule is specified by the Euler angles, the $d_{\alpha\beta}$ are not independent variables.

The Lennard-Jones term of the potential is given in the usual form:

$$V_{ij}^{\mathrm{LJ}}(r) = 4\,\varepsilon_{ij}\,[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}] \tag{2}$$

Lennard-Jones parameters for ionic interactions were obtained from the application of Kong's[7] L-J parameter combination rules to data obtained by Hogervorst[8] in the determination of the L-J parameters for the noble gases adjacent to Li and Cl in the periodic table. Values of the L-J parameters for the ion-water interactions were likewise calculated using Kong's equations and the L-J parameters for the ST2 potential. The values ε_{ij} and σ_{ij} used in the calculations are given in Table 1.

The exact form of the three Coulomb terms for the water-water, ion-water, and ion-ion interaction will be discussed separately.

The water-water Coulomb term applied here is that developed by Stillinger and Rahman[4] for their ST2 potential:

$$V_{ww}^{\mathrm{C}}(r, d_{11}, d_{12} \ldots) = S_{ww}(r) \cdot q^2 \cdot \sum_{\alpha,\beta=1}^{4} \frac{(-1)^{\alpha+\beta}}{d_{\alpha\beta}} \tag{3}$$

where $d_{\alpha\beta}$ denotes the distance between charge α on one water molecule and charge β on the other. The choice of α and β odd for positive charges and even for negative charges yields the correct sign. The switching function, $S(r)$, depending only on the interoxygen distance has been introduced to prevent an unlimited increase in the pair potential should two of the point charges overlap[1]. It is given by:

$$\begin{aligned} S_{ww}(r) &= 0\,, && r < R_{ww}^{\mathrm{L}} \\ &= (r - R_{ww}^{\mathrm{L}})^2\,(3\,R_{ww}^{\mathrm{U}} - R_{ww}^{\mathrm{L}} - 2\,r)/(R_{ww}^{\mathrm{U}} - R_{ww}^{\mathrm{L}})^3\,, && R_{ww}^{\mathrm{L}} \leqq r \leqq R_{ww}^{\mathrm{U}} \\ &= 1\,, && R_{ww}^{\mathrm{U}} < r \end{aligned} \tag{4}$$

with $R_{ww}^{\mathrm{L}} = 2.0160$ Å and $R_{ww}^{\mathrm{U}} = 3.1287$ Å[4]. In the actual calculations, the pair potential of the water-water interaction was taken to be zero beyond a cut-off distance of 7.05 Å. The Coulomb terms of the pair potentials for the ion-ion and ion-water interactions are far reaching and would involve forbiddingly long calculations to obtain the correct, instantaneous overall force on a particle. It is the aim of this paper to obtain results concerning the near surroundings of ion, inside a sphere of about 3 to 4 Å radius. It was therefore considered justified to cut short the ion- ion and ion-water pair potentials too. The cut-off distances of the ion-ion and ion-water potentials were chosen to be 9.20 Å and 8.30 Å respectively. In order to avoid abrupt changes of the forces with distance for particles situated near the cut-off spheres, a continuous dwindling of the Coulomb pair potentials at the near inside of the cut-off spheres was achieved by introducing switching functions for the Coulomb terms of the ion-ion and ion-water potentials. It was decided for convenience to use the form of the switching function $S(r)$ as defined in Eq. (4) with appropriately chosen parameters. With the introduction of the attenuation constant at large distances of 78 and its switching function S, the Coulomb terms for ion-ion and ion-water interactions are given in Eqs. (5) and (6) respectively:

Table 1. Lennard-Jones parameters used in the calculations [a].

	H_2O-H_2O	Li^+-Li^+	Cl^--Cl^-	Li^+-H_2O	Cl^--H_2O	Li^+-Cl^-
σ_{ij}	3.10	2.37	3.36	2.78	3.24	2.98
ε_{ij}	52.605	24.7996	97.7878	31.048	70.0009	28.9742

[a] Sigmas given in Angstroms and epsilons in units of 10^{-16} erg.

$$V^{\mathrm{C}}_{\substack{++\\--\\(+-)}}(r) = \underset{(-)}{+} e^2 \left(77\, S_{\substack{++\\--\\(+-)}}(r) + 1\right)^{-1} r^{-1}, \qquad (5)$$

$$V^{\mathrm{C}}_{\substack{+w\\(-w)}}\left(r, d_{\substack{+1\\(-1)}}, d_{\substack{+2\\(-2)}}, \ldots\right) = \underset{(+)}{-} \left(77\, S_{\substack{+w\\(-w)}}(r) + 1\right)^{-1} \sum_{\alpha=1}^{4} \frac{(-1)^{\alpha}\, q\, e}{d_{\substack{+\alpha\\(-\alpha)}}}. \qquad (6)$$

The parameters in $S(r)$ depend on the molecules involved in the interactions and have been scaled to the σ_{ij} values used for the five different types of interactions. For the calculations reported here the following relationships were established:

$$R^{\mathrm{L}}_{ij} = 1.5\, \sigma_{ij} \quad \text{and} \quad R^{\mathrm{U}}_{ij} = 2.7\, \sigma_{ij}.$$

The values of the σ_{ij} are given in Table 1.

Figure 2 shows the pair potentials calculated for ion-ion interactions using Eqs. (2) and (5) with values of ε and σ given in Table 1. Curve I gives the pair potential for the $\mathrm{Li^+ - Li^+}$ interaction, curve II that for $\mathrm{Cl^- - Cl^-}$ interaction, and curve III that for $\mathrm{Li^+ - Cl^-}$ interaction. The effect of the switching function is clearly visible by the sharp change in the slope at the point where the switching function "cuts in ". Figure 3 gives the pair potentials for $\mathrm{Li^+}$-water and $\mathrm{Cl^-}$-water interactions using Eqs. (2) and (6) together with values of ε and σ from Table 1. For each interaction two potential curves are given, corresponding to either the ion and dipole moment vector being colinear or the ion and the oxygen-point charge vector being colinear. While curves b and d do not necessarily represent the absolute minima of the pair potential surfaces, they do show that the minimum is shifted to larger distances when the dipole moment vector is colinear with the ion. Again the effect of the switching function is clearly evident. The circle gives a minimum of the pair potential for the water-water interaction for a rather favorable orientation according to Stillinger and Rahman [4]. These pair potentials are qualitatively similar to the potential energy surfaces determined by Clementi and Popkie [9] for $\mathrm{Li^+ - H_2O}$ and by Kistenmacher, Popkie, and Clementi [10] for $\mathrm{Cl^- - H_2O}$, although there are quantitative differences. These are due most probably to the fact that the pair potential is for ions in solution and the potential energy surfaces for ion-water bonds in the vapor phase.

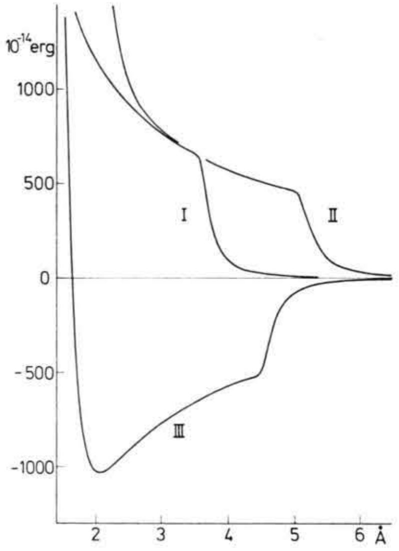

Fig. 2. Pair potentials for the ions according to Eqs. (2) and (5) with values for ε and σ as given in Table 1. Curve I: $\mathrm{Li^+ - Li^+}$; II: $\mathrm{Cl^- - Cl^-}$; and III: $\mathrm{Li^+ - Cl^-}$. The strong change in slope between 3.5 and 5.5 Å for the three curves indicates the distance at which the switching function for the Coulomb potential is "turned on".

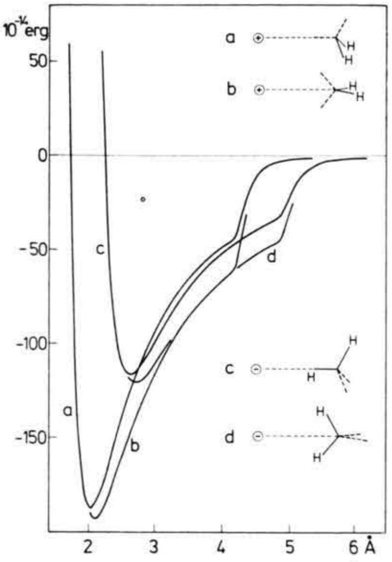

Fig. 3. Pair potentials for ion-water interactions according to Eqs. (2) and (6) with values ε and σ as given in Table 1. For both ions the potentials for two different orientations are given by the inscribed figures. The effect of the turning on of the switching function can clearly be seen. The circle gives a minimum for the water-water interactions with a rather favourable orientation.

III. Details of the Calculations

The coupled rotational and translational equations of motion were solved for the 216 particle system

($198\,H_2O$, $9\,Li^+$, and $9\,Cl^-$) using a modified version of the molecular dynamics program developed by Rahman and Stillinger[1–4]. Their program was altered to recognize the six types of pair potentials present amongst water molecules, Lithium ions, and Chloride ions. The dimensionless form of Newton-Euler equations of motion was retained and the integration performed utilizing the following integration parameters:

Mass	2.99×10^{-23} g
Length	2.82×10^{-8} cm
Energy	2.00×10^{-14} erg
Time step	$3.00 \times 10^{-4}\,\sigma(m/\varepsilon)^{1/2} = 3.27 \times 10^{-16}$ sec

The experimental density of a ca. 2 molal aqueous LiCl solution, 1.05 g/cm^3 was maintained by utilizing a periodic box having an edge length of 18.4 Å. The relatively short cut-off distances given above lead to an irreversible increase in the temperature of the solution as inferred from the average values of the translational and rotational velocities over the molecular dynamics run.

For the molecular dynamics run reported here the average temperature of the total system was maintained at 272 °K for 1080 time steps, while the total energy of the system averaged over the run was 32.8 ε. Temperature was maintained by testing the values of the velocities after each time step, stripping energy from the predictor-corrector history when the velocity became too large. (On the average, 1 of the 1836 possible adjustments was performed each time step.) Thus, the average translational temperature of the water molecules was maintained at about 300 °K, while the rotational temperature came out to be about 250 °K. The temperature of the negative ions was maintained at about 300 °K and that of the positive ions fluctuated about 250 °K. As there are only 9 ions of each type, the temperatures calculated for them are statistically suspect. This problem should disappear as one goes to a larger system and both the cut-off distances and the number of ions increase, although for an initial investigation such as this, where the feasibility of the calculation and the information obtainable about the structure of water around the ions are of primary interest, it is of secondary importance.

IV. Results and Discussion

A) Radial Pair Correlation Functions

The radial pair correlation functions $g_{\mathrm{LiO}}(r)$, $g_{\mathrm{ClO}}(r)$, and $g_{\mathrm{OO}}(r)$, giving the relative oxygen density about Li$^+$, Cl$^-$, and water molecule oxygen respectively, obtained from our molecular dynamics calculations are shown in Figures 4 – 6. Also plotted

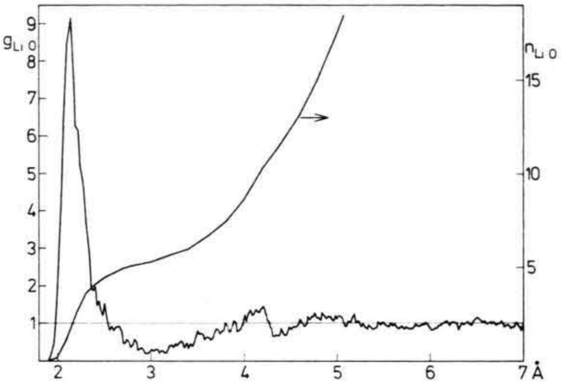

Fig. 4. Radial pair correlation function and running integration number for lithium-oxygen.

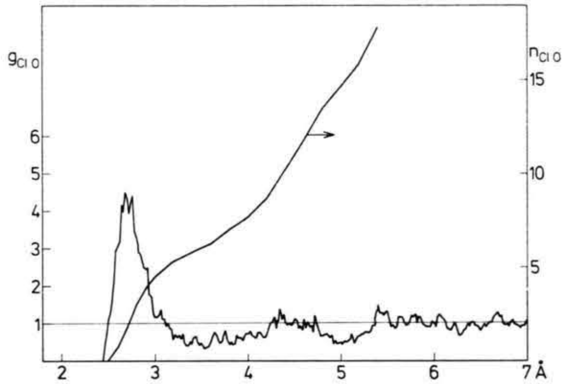

Fig. 5. Radial pair correlation function and running integration number for chlorine-oxygen.

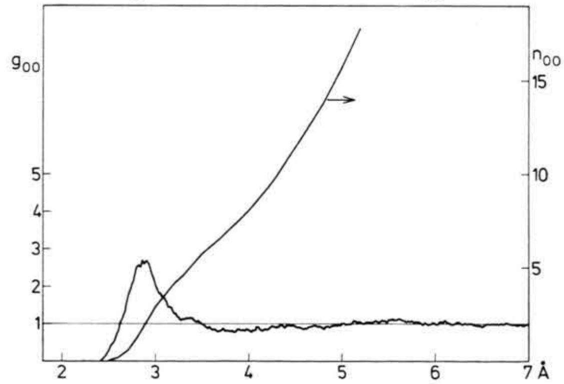

Fig. 6. Radial pair correlation function and running integration number for oxygen-oxygen.

are the running integrations of the total number of water molecule oxygens in a sphere of radius r about the central atom X, given by

$$n_{\mathrm{XO}}(r) = 4\,\pi\,\varrho_0 \int_0^r r'^2\, g_{\mathrm{XO}}(r')\,\mathrm{d}r' \qquad (7)$$

where ϱ_0 is the average number density of water molecules. The interionic g-functions are not given as there are not sufficient ion-ion interactions to yield meaningful statistics.

The number of water molecules in the first hydration sphere of an ion, or the number of nearest neighbours of a water molecule, is usually defined as $n(r)$ at the point where $g(r)$ has its first minimum. In our case this leads to a hydration number of 5.5 for Li^+ and 6.0 for Cl^-. The detailed investigations of the structure of LiCl solutions by Narten, Vaslow, and Levy[5] using X-ray as well as neutron diffraction lead to coordination numbers of 4 ± 1 for Li^+ and 6 ± 1 for Cl^-. While there is agreement for Cl^-, our calculations lead to a slightly greater number of water molecules in the first hydration sphere of Li^+. Comparing the average distances between the ions and the oxygen atoms of the first hydration sphere with the experimentally determined distances, our calculations yield a slightly larger distance for $\mathrm{Li}^+ - \mathrm{O}$ and a slightly smaller one for $\mathrm{Cl}^- - \mathrm{O}$. The maxima of the radial distribution functions occur in both cases at the same r as the maxima of the corresponding pair potentials. The discrepancies between these calculations and the experimental data are not to be taken too seriously, however, as the "noise" on the curves in Figs. 4 and 5 prevents a good determination of the minima on which the derived numbers are based. Thus, further detailed comparison between the structure data of Narten et al. and that derived from calculations of this type is not justified at this stage of the investigation and will have to wait until computed results for a larger number of ions are available. This will require a larger periodic box together with a greater number of time steps.

Because of the relatively high ion concentration in 2 molal solutions a second hydration shell is not recognizable. The sharp decline in g_{LiO} at 4.2 Å, as well as the minimum in g_{ClO} at 5.0 Å are a consequence of the strong change in the slope of the pair potentials as the switching function attenuates them, which, as noted above, is a suspect feature of this particular pair potential.

The oxygen-oxygen radial correlation function, Fig. 6, is statistically more satisfying than the ion-oxygen ones, because of the larger number of water molecules in the periodic box. It can therefore be discussed with more confidence. Although it is to be expected that at this concentration (11 water molecules for each ion) the long range structure of water is radically altered, g_{OO} strikingly resembles the g_{OO} function found by Stillinger and Rahman[4] for pure water at a temperature of 118 °C and a density of 1 g/cm^3, if one excepts the range between 3 and 4 Å. In this region the minimum is shifted to a somewhat larger r by a small bump, which is probably not a statistical artifact. The bump must be a consequence of the ion-water interactions, although it is not quite clear what interactions specifically cause it. In addition this bump causes problems in defining the number of nearest neighbours. It does not appear reasonable to count the water molecules out to 4 Å as nearest neighbours, as this would yield 7 or 8. But, on the other hand, there is no intermediate point which could be reasonably chosen. Thus, further discussion on this point will have to await a study of the concentration dependence of g_{OO}.

B) Orientation of the Water Molecules

In order to obtain information on the configuration of the water molecules about the ions the average value of the cosine of the angle Θ made by the two vectors connecting the center of mass of the water molecule with the center of mass of the ion and the oxygen of the water molecule was determined as a function of distance. Figure 7 illustrates the definition of Θ for both positive and negative

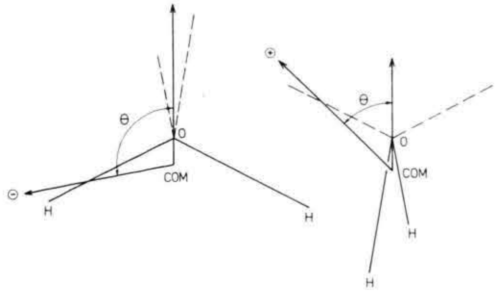

Fig. 7. Illustrations of the angle Θ between the vectors connecting the center of mass of the water molecule with the oxygen atom and the ion, the average cosine of which is shown in Fig. 8 as a function of r. The distance between the oxygen and the center of mass in the water molecule is enlarged for clarity.

ions, and the results are given in Fig. 8, where the upper portion refers to Li^+ and the lower to Cl^-. The most interesting areas of Fig. 8 are the portions between 2 and 2.5 Å for Li^+ and 2.5 and 3 Å for Cl^-, the portions coinciding with the peaks in the corresponding radial pair correlation functions, Figs. 4 and 5. In these regions the average values of $\cos\Theta$ are ca. $+0.6$ and ca. -0.6 for Li^+ and Cl^- respectively, corresponding to angles of 53° and 127°, or about half the tetrahedral angle and 180° minus half the tetrahedral angle. From the pair potential, Fig. 3, it could be expected that the dipole moment and the ion would be colinear, $\cos\Theta = \pm 1.0$, but this configuration is not obtained. Although the calculations do not allow statements about the orientation of the water molecule around the dipole moment vector, it may be inferred from the energy surface studies of Ben-Naim and Stillinger[11] that one of the electron lone pairs is pointed toward the Li^+ and one of the hydrogens toward the Cl^-. This conclusion is in close agreement with the model of Narten, Vaslow, and Levy[5] of the hydration sphere around Li^+ and Cl^- based on X-ray and neutron diffraction studies.

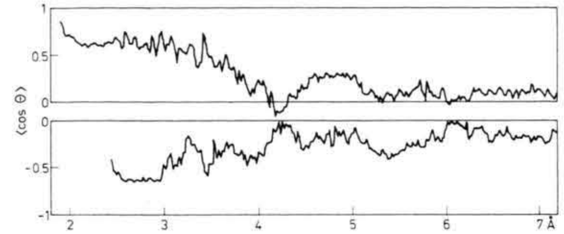

Fig. 8. The average cosine of the angle between the vectors connecting the center of mass of the water molecule with the oxygen atom and the ion as a function of the distance between ion and oxygen atom. The upper part gives the results for Li^+ and the lower part those for Cl^-.

Outside the first hydration sphere $\langle\cos\Theta\rangle$ goes to zero with increasing r, as expected when the orienting effect of the ions decreases. The minima, between 4 and 5 Å for Li^+ and between 5 and 6 Å for Cl^-, might again be a consequence of the switching function used to decrease the Coulomb potential. The increase of $\langle\cos\Theta\rangle$ in both cases for small r may be caused by another orientation being favoured at such close ion-water distances.

C) Pair Interaction Energy Distribution

Denoting the average numbers of pair interactions in the energy range dV by $p(V)\,dV$, the pair interaction energy distribution functions $p(V)$ for Li^+-water, Cl^--water and water-water are given in Figs. 9 – 11, where the ordinates are in arbitrary units. $p(V)$ increases rapidly as $V \rightarrow 0$ because of the increased numbers of interactions at large distances where Coulombic interactions are small. All of the figures show a tail in the positive region and it is interesting to note that, for both ions, this tail ends at about the same energy of 70×10^{-14} erg, as would be expected, since the tail should be dependent only on the temperature of the ions. The first hydration shell for both ions is clearly marked. Consistant with the radial distribution function curves and the result of $\langle\cos\Theta\rangle$ calculations, the low energy peaks appear at an energy which corresponds to the minimum of the pair potential in the case where the lone pair orbital and the hydrogen are directed toward Li^+ and Cl^- respectively (Figure 3). The smaller peaks at about -50×10^{-14} erg most

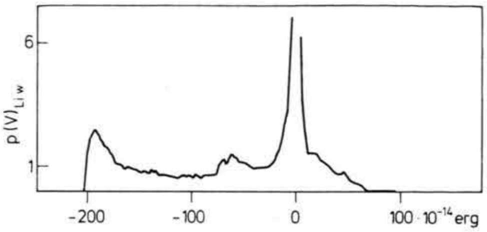

Fig. 9. Pair interaction energy distribution function for lithium-water. $p(V)_{LiW}$ in arbitrary units.

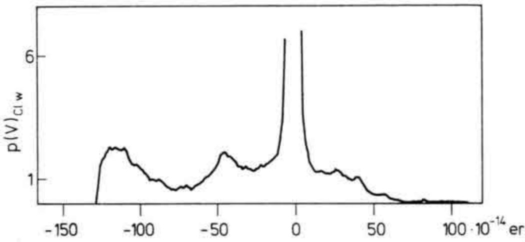

Fig. 10. Pair interaction energy distribution function for chlorine-water. $p(V)_{ClW}$ in arbitrary units.

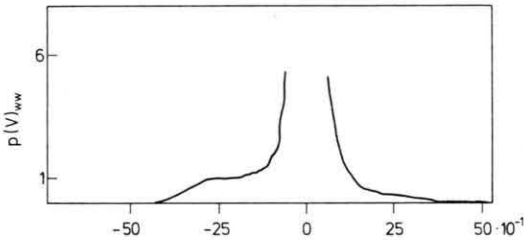

Fig. 11. Pair interaction energy distribution function for water-water. $p(V)_{WW}$ in arbitrary units.

probably have nothing to do with a second hydration shell, but seem to be a consequence of the switching function in the Coulomb part of the potential. The pair distribution function for water-water interaction energies, Fig. 11, is strikingly similar to the one found by Stillinger and Rahman[4] for pure water at 118 °C. This is again consistant with results for the radial distribution functions showing that the water-water interactions in ionic solutions resemble those in pure water at elevated temperatures, an observation for which quite some experimental evidence exists.

D) Dynamic Properties

In the discussion above it has been shown that molecular dynamics calculations applied to aqueous solutions lead to information on the static properties – restricted in these calculations to the first hydration shell – in good agreement with experimental evidence. Of course, the even more interesting aspect of such calculations is the information they can provide on the kinetic properties of the solution under investigation. Quantitative results for kinetic properties cannot be expected from this first run because of the limited statistics which are a consequence of the compromise involved in using relatively small number of particles and only a small number of time steps. But, qualitatively, even the results for the two kinetic properties calculated seem to be promising. It has been found that the diffusion coefficient calculated on the basis of the relation

$$D = \lim_{t \to 0} \left\langle \frac{[R(t) - R(0)]^2}{6\,t} \right\rangle \tag{8}$$

yields for the water molecules – not distinguishing between hydration water and bulk water – a result in the right order of magnitude as compared with experimental results.

In Fig. 12 the average of the square of the change in the Euler angles during a time step is given as a function of the distance between the ion center and the water molecule oxygen over the range of the first hydration sphere for both kinds of ions. Qualitatively, the increase of $\langle (\mathrm{d}\beta)^2 \rangle$ and $\langle (\mathrm{d}\gamma)^2 \rangle$ with decreasing distance is in agreement with experimental results of Hertz, Tutsch, and Versmold[6], who have found by NMR investigations that the water molecules in the first hydration shell of Li^+ rotate faster compared with the other water molecules. These results, together with the results for $\langle \cos \Theta \rangle$, are consistant with the following picture of a water molecule in the first hydration shell: The water molecule rotates around the dipole axis and the dipole axis itself precesses around the axis connecting the center of the ion with the center of mass of the water molecule. The angle of precession is about half the tetrahedral angle. Both rotation as well as precession increase with decreasing distance. These effects are much more pronounced for Li^+ than for Cl^-, probably because of the increased torques resulting from the closer distance of water molecule approach around the Li^+.

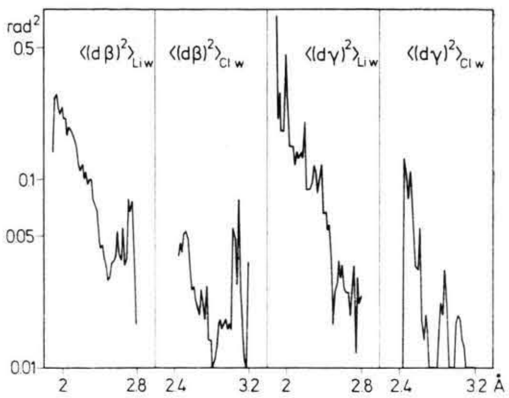

Fig. 12. Average of the square of the change in the Euler angles β and γ during a time step as a function of distance between the center of the ion and the oxygen of the water molecule. The results for both Li^+ and Cl^- are shown over the region of the first hydration shell.

V. Conclusions

The results of the study of a ca. 2 molal aqueous LiCl solution by molecular dynamics presented here are in good agreement with the static properties of the first hydration shell of Li^+ and Cl^- as determined from X-ray and neutron diffraction studies. From both, experiments and calculations, it has been concluded that in the case of Li^+ a lone pair orbital and in the case of Cl^- an H-atom of the water molecule is directed toward the ion. With respect to the calculation of kinetic properties, calculations and NMR measurements indicate a faster rotation of the water molecules in the first hydration shell of Li^+ compared with other water molecules. A model for the motion of the water molecules in the first hydration shell is tentatively proposed.

The use of the switching function in the electronic part of the pair potentials for ion-ion and ion-water interactions leads to some artificial peaks in the various properties calculated. Therefore, the switching function used in the calculations should be replaced by a more properly chosen one. As it is the aim of this investigation to show the feasibility of the calculation of properties of electrolyte solutions using molecular dynamic techniques, the calculations are restricted to 216 molecules and a limited number of time steps. This results in partially unsatisfying statistics, which means that the results obtained here are more of a qualitative nature. However, they indicated that a continuation of these calculations seems to be justified. Using an improved potential, a larger number of time steps in the 216 particle system at concentrations above 2 molal, or a system with higher numbers of particles for concentrations lower than 2 molal should yield quantitative results for LiCl.

Acknowledgements

The authors wish to express their gratitude to Drs. A. Rahman and F. Stillinger for providing us with a copy of their molecular dynamics program for our use, as well as for data on the ST2 water molecule pair potential prior to publication. We wish also to thank Professor Dr. Alfred Klemm and Dr. Lutz Schäfer for stimulating and helpful discussions during the course of the investigation.

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