

# A Molecular Dynamics Study of Aqueous Solutions

## IV. Sodium Chloride at two Different Concentrations

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Results of a molecular dynamics study of a 0.55 molal aqueous NaCl solution are reported. The basic periodic box contained 200 water molecules, 2 sodium ions and 2 chloride ions. The calculated properties of this solution are compared with those obtained previously for a 2.2 molal NaCl solution. The formation of second hydration shells, an increase of the number of water molecules in the first hydration shells, and a release of internal pressure are the main changes connected with a decrease of the concentration.

In the preceding paper<sup>1</sup> the results of a molecular dynamics study of 2.2 molal aqueous LiI, LiCl, NaCl, CsCl, and CsF solutions have been reported. In order to complete this preliminary survey of the static properties of aqueous electrolyte solutions as calculated by molecular dynamics, results on a more dilute solution are reported in this fourth paper of the series. The basic box contained 200 water molecules, 2 sodium ions and 2 chloride ions, equivalent to a 0.55 molal NaCl solution.

The effective pair potentials, the cut-off parameters, and the equilibration procedure used here are the same as the ones given in the preceding paper<sup>1</sup> for the 2.2 molal NaCl solution. From the known density a sidelength of the basic periodic box of 18.22 Å was deduced. The system was run over 7460 time steps, equivalent to a total elapsed time of 0.813 psec, at an average temperature of 300 K.

### Results and Discussion

The results of the molecular dynamics calculation of the 0.55 molal NaCl solution (denoted by b in all of the figures) shall be compared with the results for a 2.2 molal NaCl solution (a), taken from the preceding paper<sup>1</sup>. The statistics for the ion-water interactions are poorer for the lower concentration, since the number of ions is reduced by a factor of four while the number of time steps is increased by a factor of only two.

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### A) Radial Pair Correlation Functions

The radial pair correlation functions,  $g_{\text{NaO}}(r)$ ,  $g_{\text{NaH}}(r)$ ,  $g_{\text{ClO}}(r)$ ,  $g_{\text{ClH}}(r)$ , and  $g_{\text{OO}}(r)$ , and the corresponding running integration numbers  $n(r)$  for the two different concentrations are shown in Figures 1–3. Some characteristic values of the functions  $g_{\text{XO}}(r)$  are given in Table 1. The table shows that in the limits of statistical uncertainty the positions of the first maximum and the minimum of  $g_{\text{NaO}}(r)$  and  $g_{\text{ClO}}(r)$  do not depend on the concentration.  $R_2$  increases with decreasing concentration

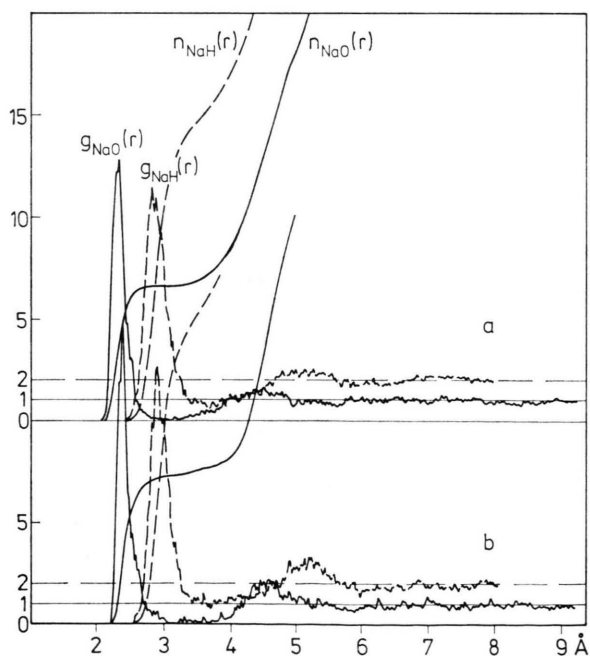


Fig. 1. Radial pair correlation functions and running integration numbers for sodium-oxygen and sodium-hydrogen in two NaCl solutions of different concentrations. a) 2.2 molal, b) 0.55 molal.



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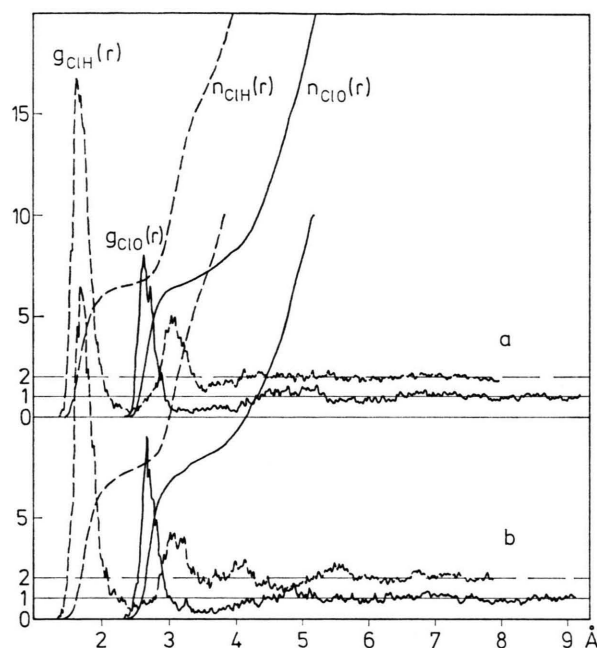


Fig. 2. Radial pair correlation functions and running integration numbers for chlorine-oxygen and chlorine-hydrogen in two NaCl solutions of different concentrations. a) 2.2 molal, b) 0.55 molal.

while  $R_1$  does not change. The maxima of the radial pair correlation functions are higher at the lower concentration, indicating a more pronounced first hydration shell and the formation of a second one. This is a consequence of a decrease in the disturbance of the hydration shells with an increase in the distance between the ions. These changes with concentration are more pronounced for the smaller ion ( $\text{Na}^+$ ) than for  $\text{Cl}^-$ . In the latter case the formation

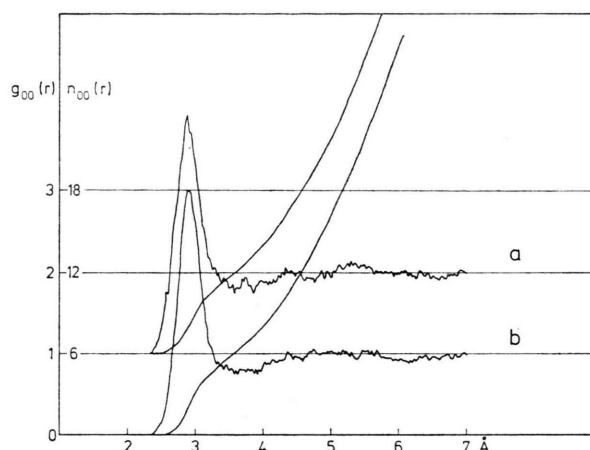


Fig. 3. Radial pair correlation function and running integration number of oxygen-oxygen in two NaCl solutions. of different concentrations. a) 2.2 molal, b) 0.55 molal.

of the second hydration shell is evident mainly by the peaks in  $g_{\text{CH}}(r)$ .

The statistical noise is too great to allow definite statements about the change of  $g_{\text{OO}}(r)$  with decreasing concentration (see Figure 3). The small bump at the minimum in a, which is supposed to be caused by the ordering of the water molecules around  $\text{Na}^+$ , has disappeared at the lower concentration, most probably because of the reduced amount of this kind of water molecules. As for the water-water interactions, the values of  $r_{\text{M1}}$ ,  $g_{\text{OO}}(r_{\text{M1}})$  and  $r_{\text{M2}}$  seem to indicate for the 0.55 molal solution properties intermediate between pure water and a concentration of 2.2 molal.

It can be seen from Figs. 1 and 2 that the hydration numbers, when defined as  $n(r_{\text{m1}})$ , are in-

Table 1. Characteristic values of the radial pair correlation functions  $g_{\text{XO}}(r)$  for two NaCl solutions of different concentrations,  $R_i$ ,  $r_{\text{Mi}}$  and  $r_{\text{mi}}$  give the distances where  $g_{\text{XO}}(r)$  is unity has a maximum and a minimum respectively. The corresponding  $g$ -values are denoted by  $g_{\text{XO}}(r_{\text{Mi}})$  and  $g_{\text{XO}}(r_{\text{mi}})$ . The values for pure water are taken from Stillinger and Rahman<sup>2</sup> by interpolating between 10 and 41 °C. The uncertainties in  $R$  and  $r$  are less than  $\pm 0.03$ , if not stated otherwise. A general statement about the uncertainties in the  $g_{\text{XO}}(r)$ -values is not possible, in each case it must be estimated from the statistical noise as shown in Figures 1–3.

X	Conc. (Moles/ kg $\text{H}_2\text{O}$ )	$R_1$ (Å)	$r_{\text{M1}}$ (Å)	$g_{\text{XO}}(r_{\text{M1}})$	$R_2$ (Å)	$r_{\text{m1}}$ (Å)	$g_{\text{XO}}(r_{\text{m1}})$	$r_{\text{M2}}$ (Å)	$g_{\text{XO}}(r_{\text{M2}})$
$\text{Na}^+$	2.2	2.14	2.31	12.77	2.57	3.11	0.011	$4.5 \pm 0.1$	1.6
	0.55	2.14	2.32	14.80	2.63	$3.10 \pm 0.15$	0.04	$4.44 \pm 0.10$	2.23
$\text{Cl}^-$	2.2	2.51	2.66	8.00	2.96	$3.40 \pm 0.10$	0.18	$5.0 \pm 0.2$	1.6
	0.55	2.48	2.68	9.00	3.03	$3.53 \pm 0.15$	0.23	4.86	1.76
O	2.2	2.63	2.90	2.96	$3.30 \pm 0.04$	$3.73 \pm 0.15$	0.74	$5.30 \pm 0.10$	1.13
	0.55	2.66	2.88	3.05	3.28	$3.75 \pm 0.15$	0.77	$5.0 \pm 0.2$	$\geq 1.08$
	pure water	2.63	2.85	3.13	3.19	3.53	0.72	4.70	1.13

creased for the lower concentration by 0.7 in the case of  $\text{Na}^+$  and by 1 in the case of  $\text{Cl}^-$  (see e.g. Bockris and Saluja<sup>3</sup>). This result is not unexpected, as at lower concentrations the formation of the hydration shells is less disturbed by neighboring ions. The stronger change of the hydration number for  $\text{Cl}^-$  is a result of the stronger influence of the counterion  $\text{Na}^+$  on the hydration shell of  $\text{Cl}^-$  than vice versa. Statistical uncertainty does not allow a definite statement about the change with concentration of the number of nearest neighbours of a water molecule.

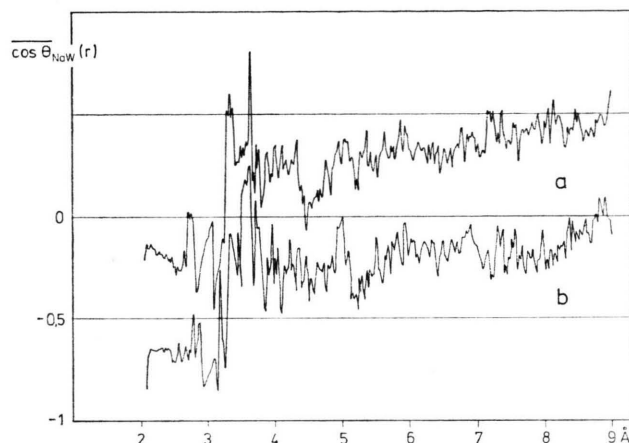


Fig. 4. Average value of  $\cos \Theta_{\text{NaW}}$  as a function of distance between sodium ion and oxygen in two NaCl solutions of different concentrations.  $\Theta_{\text{NaW}}$  is the angle between the two vectors connecting the oxygen atom with the sodium ion and with the center of mass of the water molecule. a) 2.2 molal, b) 0.55 molal.

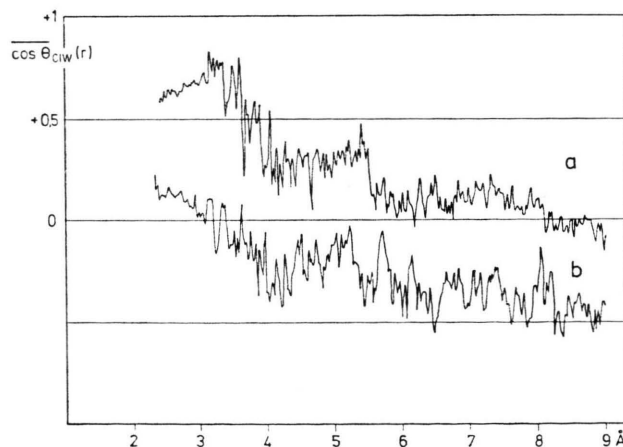


Fig. 5. Average value of  $\cos \Theta_{\text{ClW}}$  as a function of distance between chloride ion and oxygen in two NaCl solutions of different concentrations.  $\Theta_{\text{ClW}}$  is the angle between the two vectors connecting the oxygen atom with the chloride ion and with the center of mass of the water molecule. a) 2.2 molal; b) 0.55 molal.

### B) Orientation of the Water Molecules

As was the case for the 2.2 molal solution<sup>1</sup>, in the 0.55 molal solution the positions of the first peaks in the  $g_{\text{NaH}}(r)$  and the  $g_{\text{ClH}}(r)$  curves (Figs. 1 and 2) taken together with the first peaks of the corresponding  $g_{\text{NaO}}(r)$  and  $g_{\text{ClO}}(r)$  curves indicate water-ion configurations where a lone pair orbital of the water molecules is directed towards the cation and a hydrogen atom is pointed towards the anion, and the average value of  $\cos \Theta$  as a function of distance between ion and oxygen atom (Figs. 4 and 5) agrees with these configurations. There are, in the limits of statistical uncertainty, no significant differences in  $\langle \cos \Theta_{\text{IW}}(r) \rangle$  between both concentrations, except in the case of  $\text{Cl}^-$  between 3 and 4 Å, the range of the minimum of  $g_{\text{ClO}}(r)$ . It is not quite clear what causes the higher value of  $\langle \cos \Theta_{\text{ClW}} \rangle$  at the higher concentration in this range, it must be a result of the stronger orienting influence of the larger number of sodium ions.

The average value of the cosine of the angle between the dipole moment vectors of two water molecules is given as a function of oxygen-oxygen distance in Figure 6. Curves a and b are similar up to

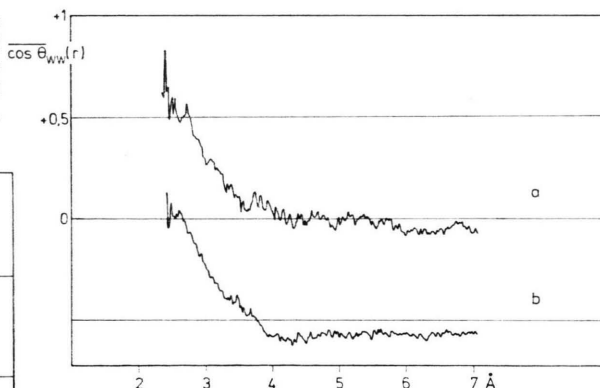


Fig. 6. Average value of  $\cos \Theta_{\text{WW}}$  as a function of distance between the oxygen atoms of two water molecules in two NaCl solutions of different concentrations.  $\Theta_{\text{WW}}$  is the angle between the dipole moment vectors of the two water molecules. a) 2.2 molal; b) 0.55 molal.

3.5 Å. For the lower concentration  $\langle \cos \Theta_{\text{WW}}(r) \rangle$  changes from positive values directly to negative values at 3.8 Å, without a range of no preferential orientation as it exists at the higher concentration between 4 and 6 Å. The slight preference for angles above  $90^\circ$  decreases very slowly with increasing

distance indicating a long range ordering of the water molecules in the 0.55 molal NaCl solution.

Denoting the unit vector in the dipole moment direction of water molecule  $i$  by  $\mathbf{m}_i$ , then  $\mathbf{M}$  is defined by

$$\mathbf{M} = \sum_i \mathbf{m}_i.$$

The quantity  $\langle M^2 \rangle / N$ , where  $N$  is the total number of water molecules in the basic periodic box, changes from 0.32 for the 2.2 molal to 0.12 for 0.55 molal solution. The value for pure ST2 water as calculated by Stillinger and Rahman<sup>2</sup> is 0.15. The small difference in  $\langle M^2 \rangle / N$  between pure water and the 0.55 molal solution, significant or not, indicates that the dipole moment correlation of the water molecules in the 0.55 molal NaCl solution is not very different from that of pure water. This longer range ordering can also be seen from  $\langle \cos \Theta_{WW}(r) \rangle$  as plotted in Figure 6.

### C) Average Potential Energy

The differences between the two concentrations in the average potential energies of a water molecule in the field of  $\text{Na}^+$  and  $\text{Cl}^-$  as a function of ion-oxygen distance, shown in Figs. 7 and 8 respectively, are not considered to be significant. This is in agreement with the only small differences in  $\langle \cos \Theta_{IW}(r) \rangle$  as plotted in Figs. 4 and 5. The fact that the differences in the average potential energies as a function of distance are not significant between

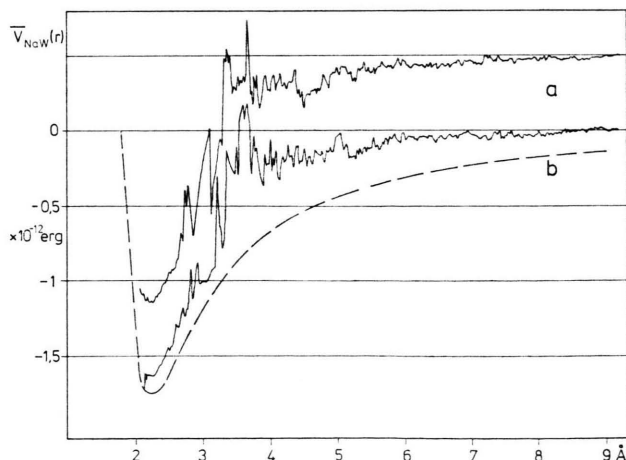


Fig. 7. Average potential energy of a water molecule in the field of a sodium ion as a function of ion-oxygen distance in two NaCl solutions of different concentrations. The broken line shows the effective pair potential for  $\cos \Theta_{\text{NaW}} = -1$ . a) 2.2 molal; b) 0.55 molal.

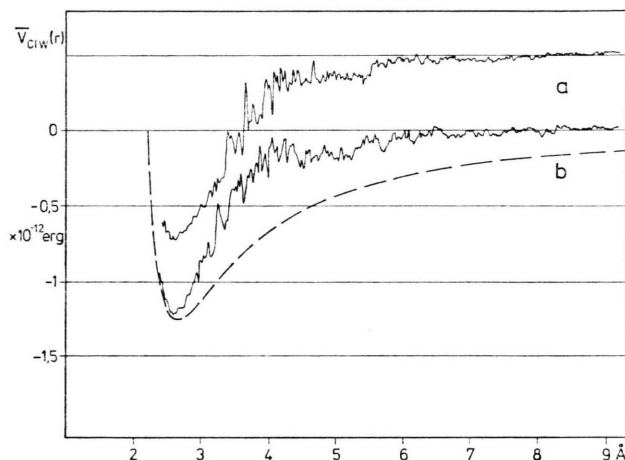


Fig. 8. Average potential energy of a water molecule in the field of a chlorine ion as a function of ion-oxygen distance in two NaCl solutions of different concentrations. The broken line shows the effective pair potential for  $\cos \Theta_{\text{ClW}} = 1$ . a) 2.2 molal; b) 0.55 molal.

both concentrations indicates that the neighbouring water molecules have a stronger influence on water molecule orientation than the ions.

In Fig. 9 the average pair potential energy of the water molecules is given as a function of oxygen-

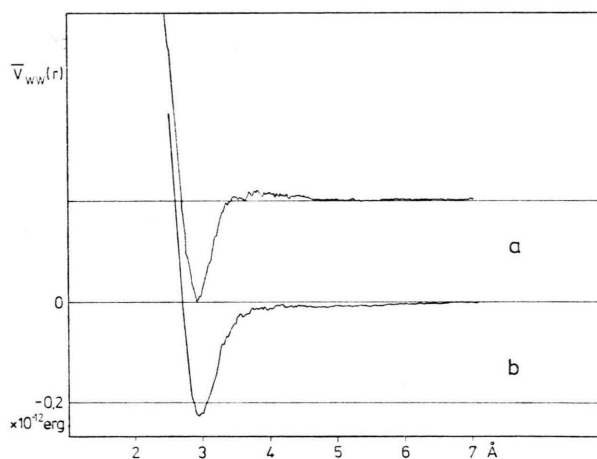


Fig. 9. Average potential energies of the water molecules as a function of oxygen-oxygen distance in two NaCl solutions of different concentrations. a) 2.2 molal; b) 0.55 molal.

oxygen distance. The obvious difference between both concentrations is the lower minimum and the disappearance of positive energies in the range between 3.5 and 4.5 Å at the lower concentration. The lower minimum is a consequence of the less disturbed water structure by the smaller number of

ions as seen above from  $\langle \cos \Theta_{\text{WW}}(r) \rangle$  and  $\langle M^2 \rangle / N$ . The disappearance of the positive energies indicates a release of internal pressure in the solutions.

#### D) Pair Interaction Energy Distribution

Denoting the average number of pair interactions having an interaction energy in the range  $dV$  by  $p(V)dV$ , the pair interaction energy distribution functions  $p(V)$  for  $\text{Na}^+$ -water,  $\text{Cl}^-$ -water and water-water are shown in Figs. 10–12 respectively for the two different concentrations.  $p(V)$  is given in arbitrary units. It increases rapidly as  $V$  goes to zero because of the greater number of interactions

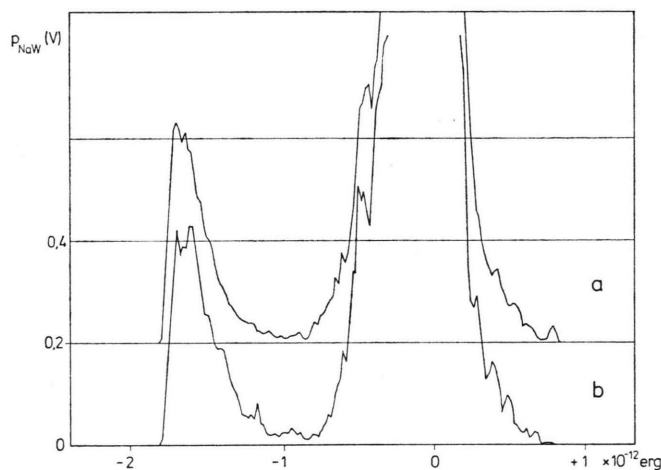


Fig. 10. Pair interaction energy distribution functions for  $\text{Na}^+$ -water in two NaCl solutions of different concentrations.  $p(V)$  is given in arbitrary units. a) 2.2 molal; b) 0.55 molal.

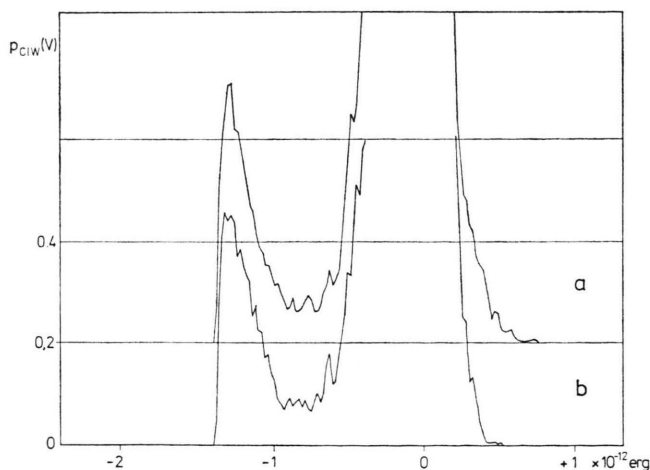


Fig. 11. Pair interaction energy distribution functions for  $\text{Cl}^-$ -water in two NaCl solutions of different concentrations.  $p(V)$  is given in arbitrary units. a) 2.2 molal; b) 0.55 molal.

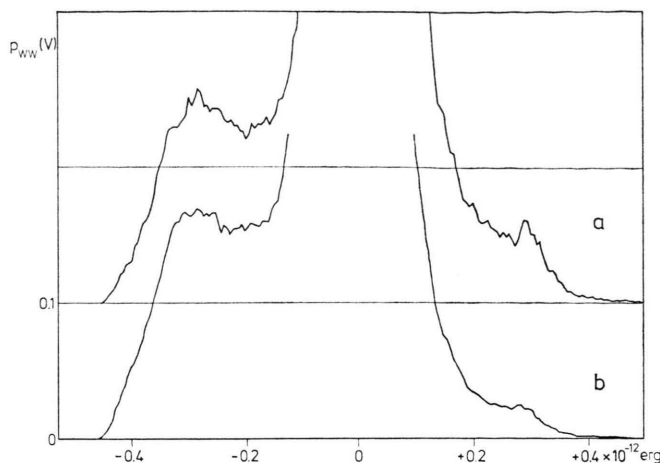


Fig. 12. Pair interaction energy distribution functions for water-water in two NaCl solutions of different concentrations.  $p(V)$  is given in arbitrary units. a) 2.2 molal; b) 0.55 molal.

at larger distances where coulombic terms of the potential are small.

While the negative energy sides of the plots in all three figures show, in the limits of statistical uncertainty, no significant differences between the 2.2 and the 0.55 molal solutions, there exist remarkable differences between curves a and b on the positive energy sides. The number of water molecules with positive energies is in all three cases smaller at the lower concentrations, a consequence of the smaller number of ions forcing less water molecules into unfavorable orientations. Comparing Figs. 10 and 11, it can be seen that this effect is more pronounced in the case of  $p_{\text{ClW}}(V)$ , because the smaller  $\text{Na}^+$  disturbs the hydration shell of  $\text{Cl}^-$  more than vice versa. The smaller number of ions allow also a more favorable orientation of the water molecules relative to each other, resulting in a strong decrease of the shoulder at about  $2.8 \cdot 10^{-13}$  erg (ca. 4 kcal/mole)<sup>5</sup>. This is an additional indication of released internal pressure at the lower concentration, an effect which is also recognizable in the property  $p/\rho kT - 1$  as calculated from the average virial of the intermolecular forces, the value of which reduces by a factor of three in going from the 2.2 to the 0.55 molal NaCl solution.

#### E) Self Diffusion Coefficient for Water

The self diffusion coefficient for the water molecules calculated here by using the relationship

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

changes from 7.9 for the 2.2 molal to  $4.4 \cdot 10^{-5}$  cm<sup>2</sup>/sec for the 0.55 molal solution, while from the NMR measurements of Endom, Hertz, Thül, and Zeidler<sup>6</sup> the corresponding values 2.0 and  $2.3 \cdot 10^{-5}$  cm<sup>2</sup>/sec can be estimated. Although the discrepancy between calculated and measured self diffusion coefficient has become remarkably smaller at the lower concentration, the still existing difference indicates

most probably that even the twice as long simulation time used here was not long enough to reach the limiting slope.

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