Structure and Dynamics of NaCl in Methanol. A Molecular Dynamics Study

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A recently developed flexible three-site model for methanol was employed to perform a Molecular Dynamics simulation of a 0.6 molal NaCl solution. The ion-methanol and ion-ion potential functions were derived from *ab initio* calculations. The structural properties of the solution are discussed on the basis of radial and angular distribution functions, the orientation of the methanol molecules, and their geometrical arrangement in the solvation shells of the ions. The dynamical properties of the solution – like self-diffusion coefficients, hindered translations, librations, and internal vibrations of the methanol molecules – are calculated from various autocorrelation functions.

I. Introduction

The investigation reported here is a continuation of the recent Molecular Dynamics (MD) simulation of a 0.6 molal $MgCl_2$ solution in methanol [1]. A three-site flexible methanol model is employed in the simulation [2] and the ion-methanol and ion-ion pair potentials are derived from ab initio calculations.

Although methanol is an interesting solvent, as its molecule has a hydrophobic and a hydrophilic group, the number of structural and dynamical studies of methanolic solutions is quite small [3]. Because of the low solubility of NaCl in methanol diffraction studies have not been reported in the literature. Therefore ion-methanol radial distribution functions (RDFs) from the MD simulation can only be compared with results of Monte Carlo (MC) calculation of Na^+ surrounded by 127 rigid methanol molecules [4] and a simulation of Cl^- in TIPS methanol [5]. Dynamical properties of the system under consideration derived from a simulation are presented here for the first time. In addition, an extended RISM analysis of a methanolic NaCl solution has ben reported by Hirata and Levy [6].

The self-diffusion coefficient of the ions and the methanol molecule in the solution have been measured by Hawlicka [7, 8] and can serve as a check on the quality of the pair potential employed in the simulation. Furthermore, from a series of IR studies of LiCl and $MgCl_2$ solutions in Methanol at low temperatures Strauss and Symons [9] evaluated the effect of Cl^- on the OH stretching frequency of the methanol molecules in its first solvation shell. The use of a flexible methanol model in the simulation and the division of all methanol molecules in the solution into three subsystems – bulk, solvation shell molecules of Na^+ and Cl^- – enables the calculation of the single ion effect on various properties of the methanol molecules, too.

The differences between methanol and water as solvent are evaluated by a comparison of the various structural and dynamical properties of the solution investigated here with those from a simulation of an aqueous NaCl solution [10]. The comparison with the results from the simulation of a methanolic $MgCl_2$ solution [1] provides information on the effect of cations on various properties of the solution.

II. Pair Potentials and Details of the Simulation

The flexible PHH model was used to describe the methanol-methanol interactions [2]. It is essentially a

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$\mathscr{C}_S$ version of the BJH water [11] where the whole methyl group is represented in the fused atom approximation as one interaction site denoted by C. Intermolecular and intramolecular parts are treated independently. The intermolecular part consists of a Coulomb term with appropriate partial charges on the sites and non-Coulombic interactions, whereas the intramolecular part consists of an anharmonic three body potential in the OH and CO stretch and the COH bend internal coordinates. The equilibrium gas phase geometry of the PHH methanol molecule ($r_{OH}=0.9451$ Å, $r_{CO}=1.425$ Å, $\alpha_{COH}=108.53°$) is the experimental one [12].

The pair potential describing the ion-methanol and ion-ion interactions are derived via *ab initio* calculations on the Hartree-Fock level. Several investigations of similar ion-solvent combinations lead to the conclusion that electron correlation [13] and three body effects [14] are not too important for the system under consideration. The closed shell RHF-SCF calculations of the Na^+-methanol, Cl^--methanol, Na^+-Na^+ and Na^+-Cl^- pair potentials were performed with the program HONDO [15, 16] in the same way as for the $MgCl_2$ solution [1]. Dunnings contracted DZP basis sets for C, H and O were used [17]. The basis sets for Na^+ (4 2 1/3 1/1*), and Cl^- (4 3 3/4 3/1*) are the Huzinaga MIDI* basis sets obtained by adding d-polarization functions and splitting the valence shells of the corresponding MINI basis sets in the case of the cations [18]. The potentials for the Cl^--Cl^- interactions are taken from [19].

As data base for the mapping of the ab initio energy surface of the ion-methanol supermolecules 630 to 650 configurations were choosen in each case. The points are distributed with decreasing density in regions of low interaction energy. The methanol molecule was kept in a fixed position in space with the staggered equilibrium geometry. The rotational barrier of the staggered-eclipsed conformations amounts to 5.4 kJ/mol with the present DZP basis set in good agreement with the experimental results of 4.5 kJ/mol obtained by Lees and Baker [12]. Having the discrete energy surfaces for the supermolecules, the following analytical form was fitted to it:

$$V_{\text{fit}}^{A-B}(\{r_{i\alpha}\}) = \sum_{\{i,\,\alpha\}} \left\{ \frac{Q_{i\alpha}}{r_{i\alpha}} + \frac{A_{i\alpha}}{r_{i\alpha}^{s_{i\alpha}}} + B_{i\alpha}\exp[-C_{i\alpha}r_{i\alpha}] \right\}, \tag{1}$$

where the indices i and α denote sites on the particles A and B, respectively. The space of the fit parameters is spanned only by $\{A_{i\alpha}, B_{i\alpha}, C_{i\alpha}\}$, the $\{Q_{i\alpha}\}$ are defined by the partial charges on the three sites of the PHH methanol molecule and the ionic charge, the multipole exponents $\{s_{i\alpha}\}$ are 6 for like ion combinations and 2 in all other cases. The final parametrization is given in Table 1, and the contour plot for Na^+ in the COH plane of the methanol molecule is presented in Fig. 1; the corresponding plot in the case of Cl^- can be found in [1]. In Fig. 2 the potential energy of the Na^+-methanol interaction for an orientation as indicated in the insertion is presented as a function of the ion-oxygen distance. The ab initio data points are well reproduced by the fitted curve with the parame-

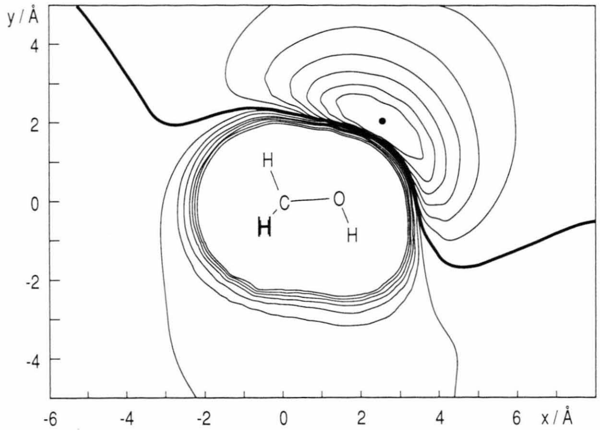

Fig. 1. Contour plot of the potential energy surface for the Na^+-methanol complex. The differences between two adjacent contour lines are 15 kJ/mol with an energy minimum at −111 kJ/mol.

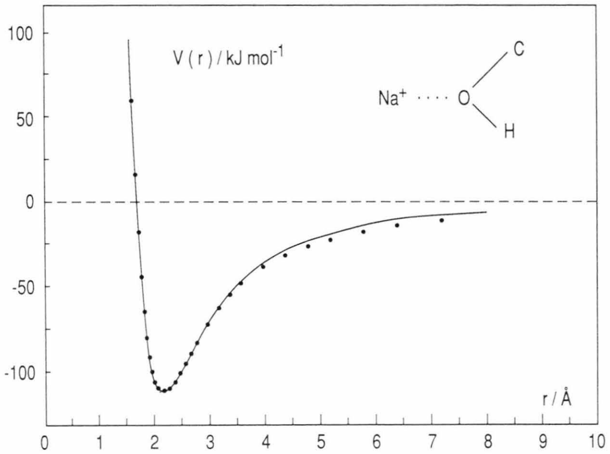

Fig. 2. Fitted Na^+-methanol potential as a function of the ion-oxygen distance for the orientation shown in the insertion. Dots indicate energy values from the ab initio calculations.

Table 1. Parameters for the ion-methanol and ion-ion potential according to (1)

i	α	$Q_{i\alpha}$ [kJ Å mol^{-1}]	$A_{i\alpha}$ [kJ Å$^{s_{i\alpha}}$ mol^{-1}]	$B_{i\alpha}$ [kJ mol^{-1}]	$C_{i\alpha}$ [Å^{-1}]	$s_{i\alpha}$	References
Na	C	347.34	−274.93	5.1664×10^4	2.7930	2	[this work]
Na	O	−833.61	−172.19	2.5323×10^5	4.1501	2	[this work]
Na	H	486.27	593.29	-8.3273×10^2	0.9591	2	[this work]
Cl	C	−347.34	6.7657	5.9250×10^5	3.2984	2	[1]
Cl	O	833.61	127.00	1.4529×10^5	3.1999	2	[1]
Cl	H	−486.27	−193.37	2.5086×10^4	3.3082	2	[1]
Na	Na	1389.4	991.35	1.0178×10^6	5.5909	6	[this work]
Cl	Cl	1389.4	−28672	9.1704×10^5	3.3863	6	[19]
Na	Cl	−1389.4	−78.985	1.7168×10^5	3.1940	2	[this work]

ters as given in Table 1. The interaction energies for the Na^+ and Cl^- complexes with methanol in the global minimum are −111 and −50 kJ/mol, respectively. It is interesting to note that calculations of Na^+–BJH water and Cl^-–BJH water complexes with exactly the same basis sets as the ones used in this work give complexation energies which differ by less 1 kJ/mol from those for the methanol complexes [20]. The maximal basis set superposition error was estimated with the help of the counterpoise method to be less than 2% of the complexation energy, which means that no counterpoise correction has to be applied in view of the error due to the non pairwise additivity of the ion-solvent potentials. In addition, there is excellent agreement in the case of the ion-ion interactions with very accurate multireference CI calculations of Clementi and coworkers [21, 22]. The energy minima of the Cl^--methanol and Cl^--water complexes lie in the COH plane in directions of the OH bond but slightly tilted towards the dipole vector of the molecule. In the case of Na^+-methanol and Na^+-water the minima fall on the anti-dipole direction of the molecule while for Mg^{2+}-methanol the minimum is slightly off this direction [1].

In the MD simulation of the 0.6 molal NaCl solution in methanol the basic cube contained 400 methanol molecules, 8 cations and 8 anions, corresponding to a sidelength of 30.13 Å. The Ewald summation was employed for all Coulombic interactions and the shifted force potential method for the non-Coulombic parts of the potentials. Due to the large simulation box used, it was possible to apply the shifted force method also to the r^{-2} terms of the potentials given by (1) with a cutoff radius of half the boxlength. The system was equilibrated for about 10 000 time steps. The simulations extended over 7.0 ps with a time step of 0.25 fs. During the simulation the velocities were not rescaled in order to get reliable velocity autocorrelation functions. The average temperature of the run was 292 K and the stability of the total energy was better than 0.5%.

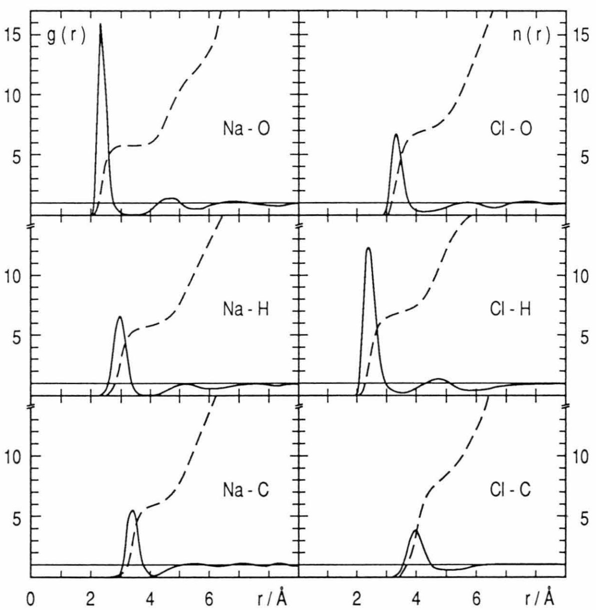

Fig. 3. Ion-oxygen, ion-hydrogen, and ion-carbon radial distribution functions and running integration numbers from an MD simulation of a 0.6 molal NaCl solution in methanol.

III. Results and Discussion

a) Radial Distribution Functions (RDFs)

In Fig. 3 the ion-oxygen, ion-hydrogen and ion-methyl partial RDFs and the corresponding running

Table 2. Characteristic values of the radial distribution functions $g_{\alpha\beta}(r)$ for the 0.6 molal NaCl solution in methanol. R_i, r_{Mi} and r_{mi} give the distances in Å, where for the i-th time $g_{\alpha\beta}(r)$ equals unity, has a maximum and a minimum, respectively. The uncertainty is at least ±0.02 Å.

α	β	R_1	r_{M1}	$g_{\alpha\beta}(r_{M1})$	R_2	$n_{\alpha\beta}(R_2)$	r_{m1}	$n_{\alpha\beta}(r_{m1})$
Na	O	2.12	2.38	15.9	2.78	5.6	3.4	5.8
Na	O[a]	2.10	2.30	8.00	2.66	(5.5)	3.10	5.8
Na	H	2.57	2.95	6.9	3.38	5.6	3.8	5.9
Na	C	3.06	3.35	5.5	3.78	5.6	4.1	6.0
Cl	O	3.02	3.28	7.0	3.80	6.5	4.3	7.2
Cl	O[a]	2.95	3.18	3.37	3.60	(6.5)	3.87	7.7
Cl	O[b]	2.95	3.28	6.5	3.72	5.9	4.2	6.6
Cl	H	2.03	2.35	12.7	2.97	6.5	3.4	7.0
Cl	C	3.53	3.88	3.9	4.48	7.4	5.0	8.6

[a] From a 2.2 molal aqueous NaCl solution [10].
[b] From a 0.6 molal $MgCl_2$ solution in methanol [1].

integration numbers from the simulation of the 0.6 molal solution of NaCl in PHH methanol are presented. The main characteristic values of the functions are summarized in Table 2. The methanol-methanol partial RDFs are very similar to the ones of pure methanol [2] and are, therefore, not displayed here.

The peaks in the Na^+-methanol RDFs are much less pronounced than the corresponding ones for Mg^{2+} [1], consistent with the larger size and smaller charge of Na^+. While the positions of the first peak in $g_{NaO}(r)$ and $g_{NaH}(r)$ are very similar to those in BJH water they are twice as high [10], a result which has to be attributed – at least partly – to the about 10% lower potential minimum in the Na^+-methanol pair potential. The solvation number for Na^+ in methanol is found to be 5.8, which is exactly the same as in water. Robinson and Symons [23] deduced from IR overtone spectroscopy a solvation number of 5.7 for Na^+ in methanol. Because of this close agreement of the solvation numbers between simulation and experiment, the number of methanol molecules in the second solvation shell, which is not accessible by experiments, may be estimated reliably from the simulation to be 6.2. The second hydration shell of Na^+ contains about twice as many molecules [10], as in the average only one hydrogen bond per methanol molecule can be formed between the first and second solvation shell but around two hydrogen bonds per hydrated water molecule. The solvation number of 5.8 results from the fact that in 80% of all cases Na^+ is solvated by 6 and in 20% by 5 methanol molecules. Compared to the position of the minimum in the Na^+-methanol pair potential the first maximum of $g_{NaO}(r)$ is shifted by 0.2 Å to larger distances. In water the same shift is less than 0.1 Å, which means that the repulsive interactions between the bulky methyl groups prevent a tighter binding of the solvated molecules. The Na^+-solvent pair potentials both in water and in methanol have their minima for an anti-dipole orientation at a Na–O distance of 2.2 Å. There is a qualitatively good agreement between the result of the present simulation and Jorgensens MC simulation of one Na^+ in 127 TIPS methanol molecules as far as can be judged from the numbers given in their paper [4].

In analogy to the cations, the first solvation shell of Cl^- is more pronounced in methanol than in water. The first peak in $g_{ClO}(r)$ is again twice as high as in water (Table 2). The separation between solvation shell and bulk molecules is sharper in methanol than in water, as can be seen from the value of $g_{ClO}(r)$ at r_{m1}, which is with 0.3 less than half of the corresponding value in water. The solvation number of Cl^- is found to be 7.2, which is similar to the hydration number of 7.7 in BJH water. The distribution of solvation numbers for Cl^- is much broader than for the cation (17, 50, and 33% for solvation numbers of 6, 7, and 8, respectively). In the methanolic $MgCl_2$ solution the solvation number of Cl^- is only 6.6. This lower value results from the contact ion pair formation in the methanolic $MgCl_2$ solution, where a Mg^{2+} occupies the place of solvent molecules and thus reduces the solvation number of the anion [1]. This effect on the coordination and solvation numbers is well known from simulations of concentrated electrolyte solutions [24]. While in the 0.6 molal $MgCl_2$ solution one out of four Mg^{2+} is engaged in contact ion pair formation, the Na–Cl RDF gives no indication for contact ion pairs. The positions of the extrema of $g_{ClO}(r)$, $g_{ClH}(r)$ and $g_{ClC}(r)$ compare well with the results from a simulation of one Cl^- in TIPS methanol

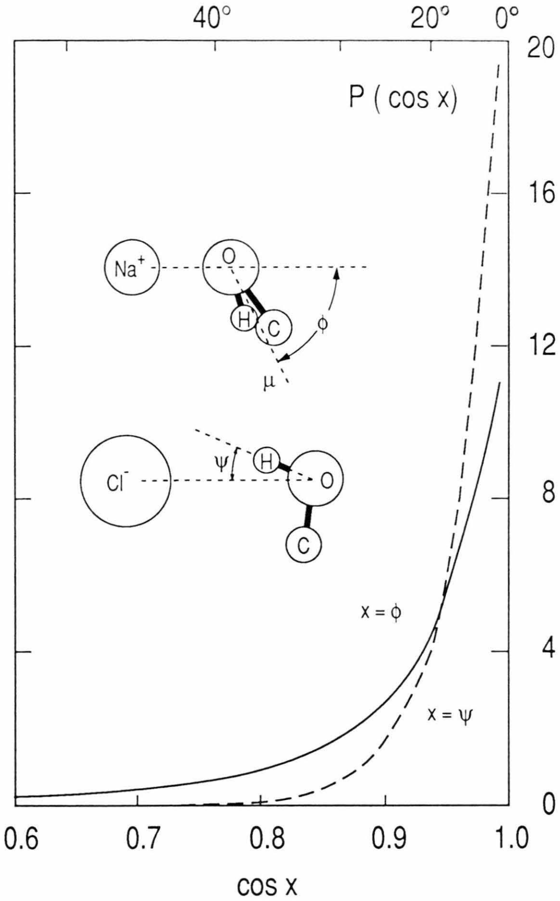

Fig. 4. Distribution of cos Φ and cos Ψ for the methanol molecules in the first solvation shells of Na^+ and Cl^-, respectively, calculated from an MD simulation of a 0.6 molal NaCl solution in methanol. μ is the dipole moment vector of the methanol molecule.

[5] although the solvation number in TIPS methanol is only ≈ 5 which compares better with spectroscopic data [23].

In most cases the positions as well as the heights of the first peaks in the ion-solvent RDFs presented here differ significantly from those of an extended RISM analysis of an NaCl solution in methanol [6]. In view of the agreement with other simulation results discussed above it is not to be expected that the discrepancies have to be attributed to this work.

b) Orientation of the Molecules in the Solvation Shells of the Ions

The orientations of the methanol molecules in the first solvation shells of Na^+ and Cl^- are described by

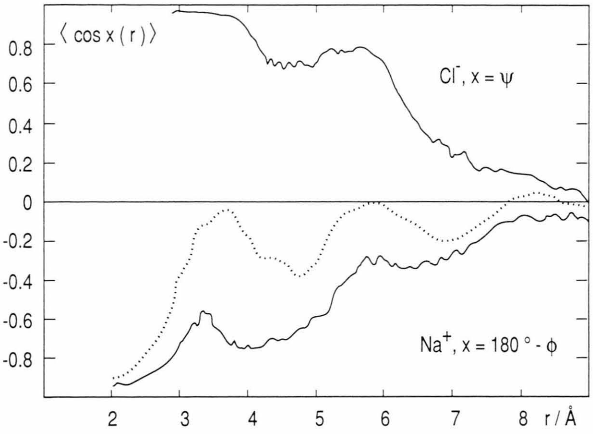

Fig. 5. Average values of cos Φ and cos $(180-\Psi)$ as functions of ion-oxygen distance, calculated from an MD simulation of a 0.6 molal NaCl solution in methanol. Φ and Ψ are defined in the insertion of Figure 4. The dotted line has been calculated from a simulation of a 2.2 molal aqueous NaCl solution [11].

the distributions of cos Φ and cos Ψ, respectively. They are shown in Fig. 4, where also Φ and Ψ are defined in the insertions. The distributions demonstrate a strong preference for a trigonal orientation of the methanol molecules surrounding Na^+ and for a linear hydrogen bond formation of the first solvation shell molecules with Cl^-. The preferential orientations are the same as in an aqueous NaCl solution [10], but they are more pronounced here in accordance with the higher and narrower first peaks in the ion-oxygen and ion-hydrogen RDFs as discussed above. The orientational effect of Mg^{2+} is significantly stronger than that of Na^+, indicated by the narrower distribution of cos Φ [1].

In Fig. 5 the average values of cos $(180-\Phi)$ and cos Ψ are presented as functions of the ion-oxygen distances. The almost monotonous decrease of the preferential orientation of the methanol molecules as a function of distance from Na^+ is interrupted only in the region between 3–4 Å. Reliable conclusions cannot be drawn from this deviation as there are only a small number of methanol molecules involved (see $g_{NaO}(r)$ in Fig. 3) and consequently the statistical significance is very limited. The situation is different for Mg^{2+} where a high degree of orientation is sustained without interruption from the first to the second solvation shell and where beyond 4.5 Å the preferential orientation slowly decreases in a similar way as for Na^+ but in general with slightly larger absolut values of cos $(180-\Phi)$ [1]. In Fig. 5 the results from an MD

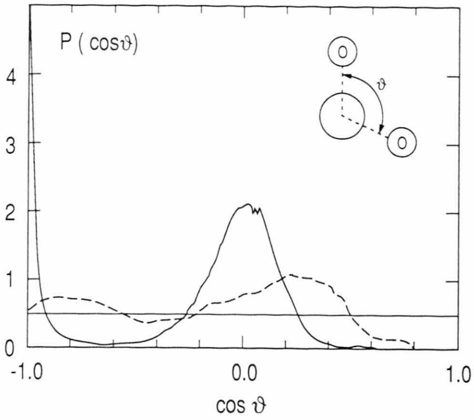

Fig. 6. Distribution of cos ϑ – where ϑ is defined as the oxygen-ion-oxygen angle – calculated for the methanol molecules in the first solvation shells of Na^+ (full) and Cl^- (dashed) from an MD simulation of a 0.6 molal NaCl solution in methanol.

simulation of a 2.2 molal aqueous NaCl solution are shown additionally for comparison [10]. The general features are very similar but the absolute values of cos (180 – Φ) are much smaller demonstrating that the orientational order around a Na^+ in water does not reach as far as in methanol and is significantly less pronounced.

The average value of cos $\Psi(r)$ – shown in the upper part of Fig. 5 – is almost one over the range of the first peak in $g_{ClO}(r)$, in agreement with the strong preference for a linear hydrogen bond formation between Cl^- and the methanol molecules in its first solvation shell. It remains high (0.7–0.8) up to about 6 Å and decreases rapidly beyond this distance. This is again a significantly farther ranging orientational order than in the aqueous case [10]. The comparison with the methanolic $MgCl_2$ solution shows that the solvation shell of Cl^- is much less disturbed in the NaCl solution at the same concentration. The reason for this difference has been attributed to contact ion pair formation in the $MgCl_2$ solution in methanol [1].

c) Solvation Shell Symmetry

The geometrical arrangement of the methanol molecules in the solvation shells of Na^+ and Cl^- has been investigated by calculating the distribution of cos ϑ, shown in Fig. 6, where ϑ is defined in the insertion. The solvation shell of the cations is octahedrally structured, as demonstrated by the maxima at 90 and 180°. As the volume of the first solvation shell – defined by r_{m1} – is smaller for Mg^{2+} than for Na^+ but has to accomodate the same number of methanol molecules, the sterical hinderance of the methyl groups prohibits larger deviations from the octrahedral geometry and more pronounced maxima [1]. For the first solvation shell of Cl^- with its 7.2 methanol molecules no symmetry is found. $P(\cos \vartheta)$ shows a practically uniform distribution over the whole range except for the excluded volume effect for cos $\vartheta > 0.8$, which results from the finite size of the methanol molecules.

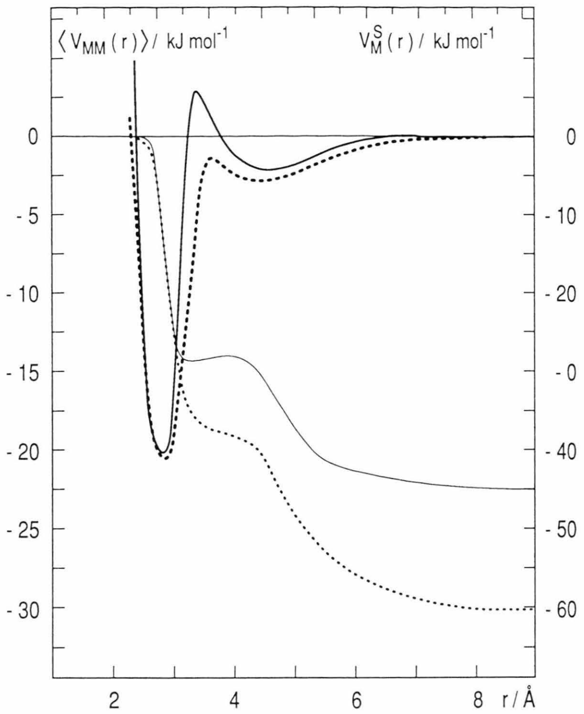

Fig. 7. Average potential energies of two methanol molecules as functions of their O–O distance and running integrated interaction energies according to (2) for the methanol molecules in a 0.6 molal NaCl solution (full) and in pure methanol (dashed).

d) Interaction Energies

The average energy of two methanol molecules as a function of their O–O distance, $\langle V_{MM}(r)\rangle$, and of a methanol molecule in the field of a Na^+ and Cl^- as a function of the ion–O distance $\langle V_{IonM}(r)\rangle$, are presented in Figs. 7 and 8. The integrated interaction energies, as defined by

$$V_\alpha^S(r) = 4\pi\, \varrho_M \int_0^r g_{\alpha O}(r)\, \langle V_{\alpha M}(r)\rangle\, r^2\, dr, \qquad (2)$$

are drawn additionally. ϱ_M is the number density of the methanol molecules and α denotes either a methanol molecule or one of the ions.

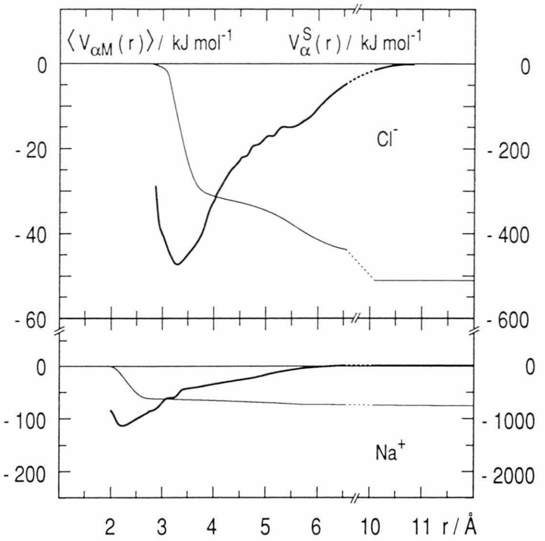

Fig. 8. Average potential energy of a methanol molecule in the field of a chloride ion (top) and a sodium ion (bottom) together with the running integrated interaction energies according to (2) calculated from a simulation of a 0.6 molal NaCl solution in methanol.

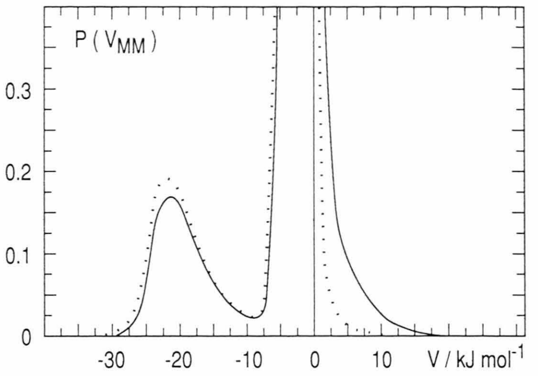

Fig. 9. Normalized pair interaction energy distributions for methanol-methanol from simulations of a 0.6 NaCl solution (full) and pure methanol (dashed).

The methanol-methanol energetics in the NaCl solution are very similar to the ones in pure methanol [2] and quite different from those in the $MgCl_2$ solution (see [1]). Obviously the 0.6 molal NaCl disturbs the methanol structure much less than the $MgCl_2$ solution at the same concentration. The positive energies at ≈ 3.5 Å result from methanol molecules in the first solvation shells of Na^+ which are forced by the ion into energetically unfavorable orientations relative to each other. A second minimum in $\langle V_{MM}(r)\rangle$ exists around 4.6 Å which almost coincides with the second peak in $g_{OO}(r)$ and an energetically favorable orientation of two methanol molecules in this distance range (see Figs. 6 and 8 in [2]). The relatively small disturbance of the solvent structure by Na^+ and Cl^- leads to a reduction of the integrated interaction energy by only 25%, which is much less than for the $MgCl_2$ solution where the reduction amounts to about 60% [1].

The average potential energies of the methanol molecules in the field of the ions and their integrated interaction energies are depicted in Figure 8. The positions of the minima in the $\langle V_{\alpha M}(r)\rangle$ coincide with those of the first peaks in the corresponding RDFs. It indicates that there is no steric hindrance between the methanol molecules in the first solvation shells of the ions which could prevent them from occupying the energetically most favorable distances. In spite of the long range orientational order – which prevents $V_\alpha^S(r)$ from reaching its limiting value even at 10 Å – the first solvation shell contributes more than half of the total integrated interaction energies for both ions.

The pair interaction energy distribution for methanol-methanol interactions in the 0.6 molal NaCl solution is compared in Fig. 9 with that for pure methanol [2]. At the negative energy side both distributions are very similar, indicating that the hydrogen bond structure of methanol is disturbed only slightly in the solution. The enhancement of the probability density in the range of positive interaction energies in the NaCl solution is a consequence of the energetically unfavorable relative orientation of two methanol molecules in the solvation shells of the ions.

The ion-methanol pair interaction energy distributions, $P(V_{\text{IonM}})$, are depicted in Figure 10. The positions of the peaks at the negative energy side practically coincide with the minima in the pair potentials. The narrowness of the distributions is in accordance with the narrow distributions of the orientations of the methanol molecules in the first solvation shells of the ions as shown in Figure 4. The weak second solvation shell of Na^+, which can be seen from $g_{NaO}(r)$ in Fig. 3, appears also from an energetical point of view as a shoulder at about -30 kJ/mol. In the case of Mg^{2+} the second solvation shell leads even to a separate peak [1].

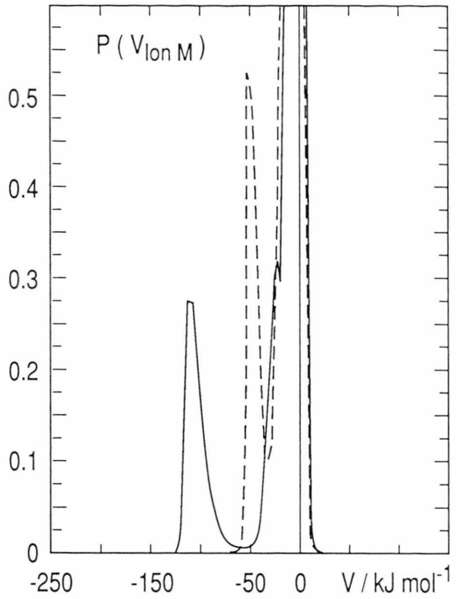

Fig. 10. Normalized pair interaction energy distributions for Na^+-methanol (full) and Cl^--methanol (dashed) from a simulation of a 0.6 molal NaCl solution.

e) Self-Diffusion Coefficients

The self-diffusion coefficients have been derived from the velocity autocorrelation functions via the Green-Kubo relation:

$$D = \lim_{t \to \infty} \tfrac{1}{3} \int_0^t \langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle \, \mathrm{d}t \,, \tag{3}$$

where the averages are calculated according to

$$\langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle = \frac{1}{N_T N} \sum_{i=1}^{N_T} \sum_{j=1}^{N} \boldsymbol{v}_j(t_i) \cdot \boldsymbol{v}_j(t_i + t) \tag{4}$$

and where N denotes the number of particles, N_T the number of time averages and $\boldsymbol{v}_j(t)$ the velocity of particle j at time t.

The normalized velocity autocorrelation functions for the ions and for the center of mass of all the methanol molecules in the 0.6 molal NaCl solution are shown in Figure 11. In addition, they have been calculated separately for the three methanol subsystems in the solution, namely bulk methanol and the methanol molecules in the first solvation shells of Na^+ and Cl^-, in order to study the single ion effect on the translational motions of methanol and are depicted in Figure 12. The first solvation shells are assumed to extend to the first minima in the corresponding ion-oxygen RDFs. As a compromise between good statistics and a long correlation time, 1.3 ps were used to calculate the self-diffusion coefficients. The velocity autocorrelation functions have decayed to zero except for statistical noise at this time, as the examination of a correlation of 2.4 ps showed. The statistical error of the self-diffusion coefficients is estimated to be $\pm 0.2 \cdot 10^{-5}$ cm²/s. For a better comparison of the

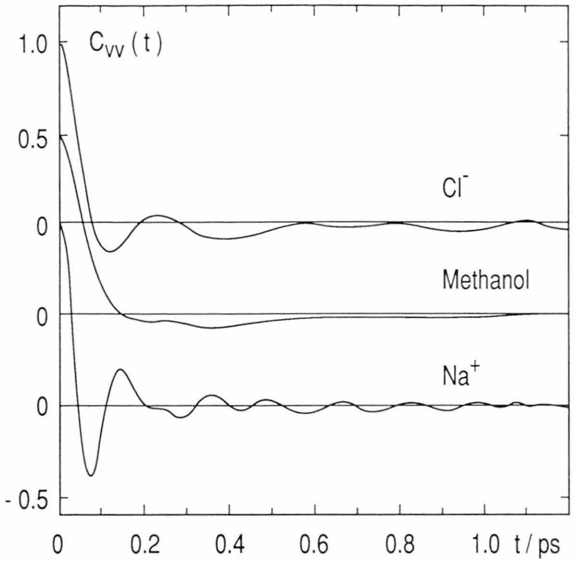

Fig. 11. Normalized velocity autocorrelation function $\langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle / \langle \boldsymbol{v}(0)^2 \rangle$ for the methanol molecules (center of mass), the sodium ions, and the chloride ions, calculated from an MD simulation of a 0.6 molal NaCl solution in methanol.

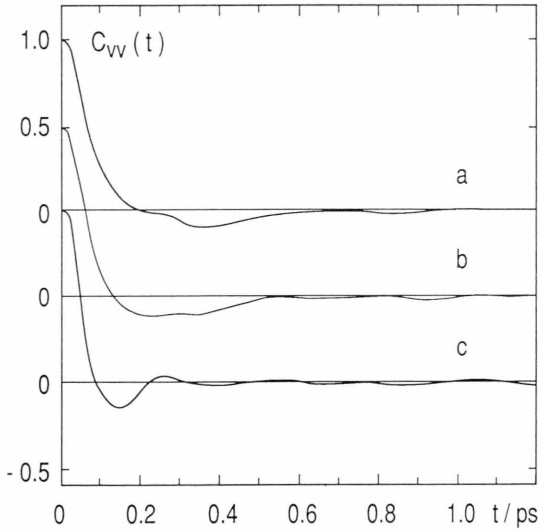

Fig. 12. Normalized velocity autocorrelation functions for the methanol molecules (center of mass), calculated from an MD simulation of a 0.6 molal NaCl solution separately for bulk methanol (a) and the methanol molecules in the first solvation shells of Cl^- (b) and Na^+ (c).

data with experimental ones and those from simulations of an aqueous NaCl solution, all self-diffusion coefficients have been extrapolated to 298 K with the help of the experimentally determined temperature dependences [25]. It should be mentioned that because of the small Stokes radius of the 3-site PHH methanol model the calculated self-diffusion coefficients for methanol are expected to be about 30% larger than the experimental ones [2] in accordance with the self-diffusion coefficient calculated from the simulation of the six-site PHH methanol model [26].

The self-diffusion coefficient for the sodium ions, $D_{\mathrm{Na}^+} = 1.2 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$, is in very good agreement with the measured value for infinitely dilute NaCl solutions in methanol of $1.22 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ [7]. The self-diffusion coefficient of the methanol molecules in the first solvation shell of Na^+ is about 50% larger than that of the ion itself. This shows the much weaker Na^+-methanol interaction than in the Mg^{2+}-methanol case where the self-diffusion coefficients of the ion and that of the solvation shell molecules are the same in the limits of statistical uncertainty [1]. The remaining influence of the Na^+ on the mobility of its solvation shell molecules remains significant when the self-diffusion coefficient is compared with that of bulk methanol, which has been calculated to be $2.7 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$. While the self-diffusion coefficients of the three methanol subsystems are not accessible experimentally, the value for all solvent molecules in the 0.6 molal NaCl which is with $2.6 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ slightly lower than that for bulk methanol compares favorably with the experimental one of $2.23 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ for a 0.16 molal NaCl solution [8].

The value of $D_{\mathrm{Cl}^-} = 0.9 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ from the simulation of the 0.6 molal NaCl solution can be compared with a measured one of $1.1 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ for a 0.013 molal solution [7]. There is a further decrease with increasing NaCl concentration expected from the experiments but an extrapolation to significantly higher concentrations seems not to be warranted because of a lack of data. The self-diffusion coefficient for the methanol molecules in the first solvation shell of Cl^- is found to be $1.6 \cdot 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$. Similar to the effect of Na^+ on its solvation shell molecules this value is significantly larger than that of the ion itself but much smaller than the one for bulk methanol.

f) Hindered Translations

The spectral densities of the hindered translational motions have been calculated by Fourier transformation,

$$f(\omega) = \int_0^\infty \frac{\langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle}{\langle \boldsymbol{v}(0)^2 \rangle} \cos(\omega t)\, \mathrm{d}t\,, \tag{5}$$

from the normalized velocity autocorrelation functions as shown in Figs. 11 and 12 and are presented in Fig. 13 for Na^+, Cl^- and, separately, for the methanol molecules in the bulk and the solvation shells of Na^+ and Cl^-.

The Cl^- spectrum shows – similar to the MgCl_2 solution – a double peak with maxima at 35 and $125\ \mathrm{cm}^{-1}$. In accordance with the assignment in the case of aqueous solutions [27] the low frequency peak can be attributed to the motion of the bare anion while interactions of Cl^- with its neighbourhood lead to the peak at the higher wavenumber. Different from the aqueous case, where the second peak is reduced to a shoulder, the same height of both peaks demonstrates again that the interactions of Cl^- with methanol are significantly stronger than with water.

The main peak in the spectrum of the hindered translations of Na^+ appears at $200\ \mathrm{cm}^{-1}$ with a small satellite peak at $260\ \mathrm{cm}^{-1}$. Because of the stronger Na^+–methanol compared with the Cl^--methanol interactions none of these frequencies can be assigned to the motion of the bare Na^+. For Mg^{2+} a single peak has been found at $450\ \mathrm{cm}^{-1}$, reflecting the hindered translational motion of this ion in the cage of the firmly attached six methanol molecules in its first solvation shell [1].

The maxima in the spectral densities of the hindered translations of the methanol molecules in the bulk and in the solvation shells of Cl^- and Na^+ appear at 35, 50, and $130\ \mathrm{cm}^{-1}$, respectively. The small difference in the position of the maxima as well as the strong similarity in the whole range of the spectral densities for bulk methanol and the methanol molecules in the first solvation shell of Cl^- (Fig. 13) are in accordance with the conclusion drawn above from most of the properties discussed that the Cl^- has only a small influence on the properties of its surrounding methanol molecules. The Na^+ causes not only an almost $100\ \mathrm{cm}^{-1}$ blueshift of the maximum but results also in a very broad distribution in the spectral densities which is very similar in shape to the one found for the solvation shell molecules of Mg^{2+} except that in the Mg^{2+} case the maximum is shifted by about $200\ \mathrm{cm}^{-1}$ relative to bulk methanol.

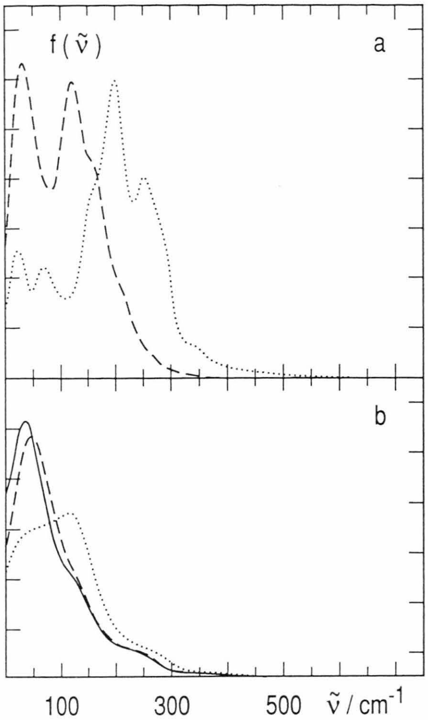

Fig. 13. Spectral densities of the hindered translations (a) of the sodium ion (dotted) and the chloride ion (dashed) and (b) of the methanol molecules, calculated separately for bulk methanol (full) and the methanol molecules in the first solvation shells of Cl^- (dashed) and Na^+ (dotted) from an MD simulation of a 0.6 molal NaCl solution in methanol and given in arbitrary units.

g) Librations and Intramolecular Vibrations

The total spectral densities in Fig. 14 are calculated as the mass weighted sum of the Fourier transforms of the velocity autocorrelation functions of the individual sites in the methanol molecule [2]. The PHH model is known to reproduce the measured IR frequencies of the three normal modes (OH stretch, CO stretch and COH bend) and describes correctly their frequency shifts from the gas phase to the liquid. Therefore it is expected that the model is able to describe reasonably well also the influence of the ions on the intramolecular properties of the solvent molecules.

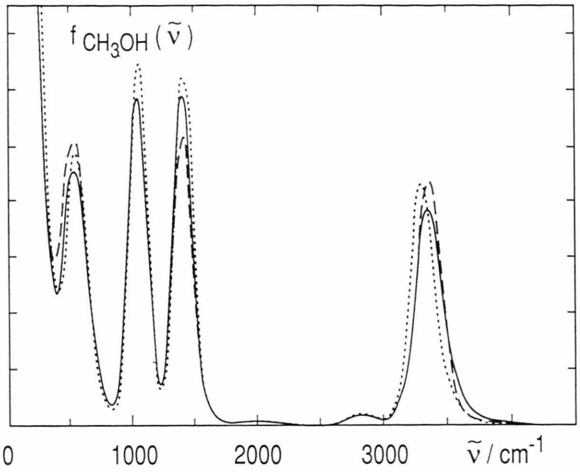

Fig. 14. Total spectral densities of liquid methanol, calculated separately for the molecules in the bulk (full), in the first solvation shells of Cl^- (dashed) and Na^+ (dotted) from an MD simulation of a 0.6 molal NaCl solution and given in arbitrary units.

In order to study the single ion effect on the intramolecular geometry, the librations and vibrations, the 400 methanol molecules are again devided into three subsystems – bulk methanol and methanol molecules in the first solvation shells of Na^+ and Cl^-. In the limits of statistical uncertainty of about $\pm 20\ cm^{-1}$, the spectral densities of the librations as well as those of the CO stretching and COH bending vibrations are not affected by Na^+ and Cl^-, as can be seen from Figure 14. But the Na^+ shifts the OH stretching frequency of its solvation shell molecules to the red by about $50\ cm^{-1}$ relative to pure methanol. This is much less than the $350\ cm^{-1}$ redshift caused by Mg^{2+} [1]. In the case of Cl^- a blueshift of about $25\ cm^{-1}$ has been calculated from the simulation. This small difference would hardly be considered significant if there would not be strong indications for such a blueshift caused by Cl^- from IR measurements of LiCl and $MgCl_2$ solutions at a temperature of −125 °C by Strauss and Symons [9]. The difference between the experimental blueshift of $100\ cm^{-1}$ and the $24\ cm^{-1}$ calculated from the simulation may have to be attributed, at least partly, to the low temperature at which the experiments were performed.

In accordance with the small effect of Na^+ and Cl^- on the vibrations, the changes caused by the ions on the intramolecular geometry of the methanol molecules in their first solvations shells do not exceed significantly the limits of statistical uncertainty.

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