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MD Simulation Studies of Selective Solvation in Methanol−Water Mixtures: An Effect of the Charge Density of a Solute

Ewa Hawlicka* and Dorota Swiatla-Wojcik

Institute of Applied Radiation Chemistry, Department of Chemistry, Technical University, Zeromskiego 116, 90-924 Lodz, Poland

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MD simulations have been performed for NaCl, NaI, and fictitious solutions of discharged counterparts of Na^+ and Cl^- ions to investigate an effect of the charge density of a solute on its solvation in methanol−water mixtures. Solvent−solvent interactions have been described in terms of flexible models, whereas solutes have been considered as charged or uncharged Lennard-Jones spheres. An analysis of solvation shells has been based on radial distribution functions, angular distributions, coordination numbers, and residence times of solvent molecules. Preferential solvation of anions by methanol molecules becomes less pronounced with decreasing charge density of a solute and vanishes for the discharged chloride ion. In contrast to preferential hydration of Na^+ in water deficit solvents, its uncharged counterpart Na^0 is preferentially solvated by methanol molecules over the whole range of solvent composition. Results for NaCl solution have been compared with those obtained with ab initio ion−solvent potentials and the same model of solvent molecules. The type of ion−solvent potential has small effect on the structure and composition of ionic shells, but its influence on the persistence of the coordination shells is more noticeable.

1. Introduction

Understanding solvation of ions in binary solvents is of fundamental importance for solution chemistry. Various experimental techniques have been employed to investigate the surrounding of the ion in solution, but a lack of theory renders even the term “preferential solvation” misleading. This qualification has been introduced to describe nonlinear variation of solution properties with the composition, but now it is commonly used to emphasize any deviation of the composition of coordination shells from that of the solvent. Preferential (selective) solvation is usually expected if a solute interacts more strongly with one of the solvent components. In a nonideal mixture, however, these compositions may differ because of the nonadditive molar volume of the solvent. In that case, to decide whether any preferences occur, composition of ionic shells should be compared with an expected content of solvation layers. This expected composition can be estimated from an appropriate ratio of solvation numbers in one-component solvents recalculated according to the component number density in the mixed solvent.[1]

Though preferential solvation is usually expected if a solute interacts more strongly with one of the solvent components, there are experimental clues that it may be a consequence of a microheterogeneity of the solvent.[2,3] The methanol−water mixture is one of the binary solvents where a microheterogeneity of the structure is believed to exist. The experimental studies on transport processes in methanol−water mixtures[3−6] as well as MD simulations[1,7−9] showed that the structure of this binary solvent does not change smoothly with increasing methanol content. A small amount of methanol, below 10 mol %, enhances the tetrahedral structure of water, because methanol molecules occupy the interstitial cavities. The enhancement of the structural order of water by a small amount of alcohol has been also postulated in NMR,[10,11] X-ray, and neutron scattering[12] measurements. With increasing methanol concentration water molecules prefer to have water neighbors, despite the fact that in the gas phase the methanol−water complex is energetically more favorable.[13] The lifetime of water globules in that binary solvent increases with methanol concentration and particularly long-living water aggregates are observed in methanol-rich solvents. Methanol preserves most of its chainlike structure if water concentration does not exceed 30 mol %.[1,7] With increasing water content methanol molecules prefer to have water neighbors, but the lifetime of this neighborhood is very short.[1,7] Thus, above 30 mol % of water concentration, the binary solvent can be treated as a mixture of water globules and methanol monomers with short-lived hydration shells.

Several experimental and computer simulation studies on methanol−water solutions of alkali halides have indicated preferential solvation of ions in these systems. NMR relaxation studies indicated preferential hydration of sodium ions in water-deficit solvents,[13,14] whereas for chloride ions either preferential solvation by methanol[14] or preferential hydration[15] was reported. In self-diffusion measurements[16] selective solvation by methanol was found for halide ions, while for alkali ions preferential hydration in methanol-rich solvents was observed. Similar preferences have been found in our MD simulation studies on NaCl−methanol−water systems.[1,8,17−19] Compared to the expected content of the solvation shell, a clearly higher concentration of methanol in the vicinity of Cl^- was obtained over the whole range of the composition. Concentration of methanol in the solvation shell of Na^+ was close to the expected content. An exception was methanol-rich solvent where Na^+ shells contained more water molecules than expected, thus showing preferential hydration. The preferences observed for Na^+ and

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* Corresponding author. Tel.: (+48-42) 6313195, Fax: (+48-42) 6365008. E-mail: hawlicka@ck-sg.p.lodz.pl.

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Cl^- ions suggest that selective solvation results from the solvent structure rather than from the ion−solvent interactions, which are similar for both solvent components.

The aim of the present work is to confirm the hypothesis[17−19] that the selective solvation in highly associated liquids is induced by solvent−solvent interactions. We examine how preferences in solvation are affected by the charge density of a solute and to what extent they depend on ion−solvent potentials used in MD simulation. Simulations presented in this paper have been performed for methanol−water solutions of sodium halides, NaCl, and NaI, and fictitious solutions of uncharged spheres of the same sizes as the Na^+ and Cl^- ions. If solvent−solvent interactions induce selectivity, the preferences should be insensitive to the ion−solvent potentials employed. The most common description of ion−solvent interactions is the Coulomb term combined with the Lennard-Jones potential.[20−25] In our previous simulations of NaCl solutions[1,8,17−19] we used the pair ion−solvent potentials, called ab initio hereafter, obtained from the ab initio potential energies fitted to the analytical form[17,26]

$$V(r) = \sum_{j=1}^{3} \frac{Q_j}{r_j} + \sum_{j=1}^{3} \frac{A_j}{r_j^2} + \sum_{j=1}^{3} B_j \exp(-C_j r_j) \qquad (1)$$

where r_j denotes distance between ion and solvent site. In the present paper, ions and their discharged counterparts have been considered as Lennard-Jones spheres, charged and uncharged, respectively, whereas solvent−solvent interactions have been described, as previously.[1,8,17−19]

2. Pair Potentials

In all simulations the water molecule was described by the flexible BJH potential.[27] The BJH potential is more complex than other flexible models,[28,29] but it is fully consistent with the PHH flexible model adopted for the methanol molecule.[30] The BJH and PHH potentials are known to reproduce the structure, energies and dynamic properties of methanol−water mixtures.[1,8,13,31,32]

In the assumed models, solvent molecules are treated as three-site bodies. In water molecules the partial charges are located on the oxygen (−0.66 e) and the hydrogen (+0.33 e) atoms. Methanol molecules consists of the charged oxygen (−0.6 e), hydroxyl hydrogen (+0.35 e), and the methyl group (+0.25 e), considered as the pseudo-atom. Non-Coulomb terms describing the O−O, O−H, and H−H interaction of methanol and water molecules have been taken from the modified CF model for water.[33] The non-Coulomb interaction of the methyl group with the hydroxyl hydrogen has been neglected, and that with the other molecular sites represented by the Lennard-Jones (LJ) type potential.[34]

All ion−solvent and ion−ion interactions have been expressed by the sum of pair potentials consisting of the Coulomb and LJ non-Coulomb terms:

$$V_{ij}(r) = \frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \qquad (2)$$

Non-Coulomb parameters of the pair potential in eq 2 have been calculated according to the standard combining rules:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \cdot \epsilon_{jj}} \text{ and } \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad (3)$$

where ϵ_{ii} and σ_{ii} stand for the LJ parameters taken from ref 23 for ions and water, and from ref 34 for methanol. Coulomb and non-Coulomb parameters of the assumed ion−ion and ion−solvent potentials are summarized in Table 1.

TABLE 1: Parameters Q_{ij}/(kJ·nm·mol^{-1}), A_{ij}/(kJ·nm^{12}·mol^{-1}), and B_{ij}/(kJ·nm^6·mol^{-1}) of the Ion−Ion and Ion−Solvent Pair Potentials Given by Eq 2 (see text)

ion	site	Q_{ij}[a]	$A_{ij} \times 10^6$	$B_{ij} \times 10^3$
Na^+	O_M	−83.374	0.6681	1.1807
	H_M	+52.695	0	0
	CH_3	+34.739	4.327	3.598
	O_W	−91.628	0.6681	1.1807
	H_W	+45.815	0	0
	Na^+	+138.96	0.145	0.493
	Cl^-	−138.96	5.459	3.021
	I^-	−138.96	10.310	4.151
Cl^-	O_M	+83.374	18.038	6.135
	H_M	−52.695	0	0
	CH_3	−34.739	162.04	19.140
	O_W	+91.628	18.038	6.135
	H_W	−45.815	0	0
	Cl^-	+138.96	88.038	12.130
I^-	O_M	+83.374	57.35	10.94
	H_M	−52.695	0	0
	CH_3	−34.739	249.93	29.50
	O_W	+91.628	57.35	10.94
	H_W	−45.815	0	0
	I^-	+138.96	609.71	31.93

[a] Calculated using the BJH and PHH models of water and methanol, respectively.

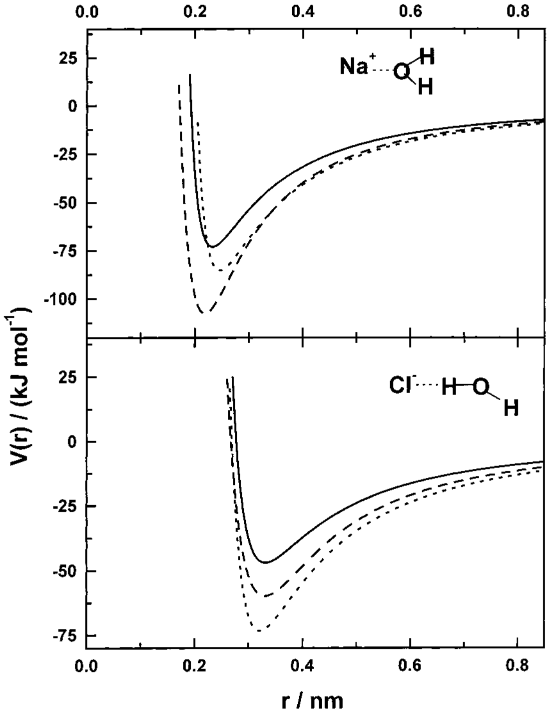

Figure 1. Potential energies of Na^+−water (upper panel) and Cl^-−water (lower panel) complexes as a function of the ion−oxygen distance. LJ potentials: BJH water (solid lines) and SPC/E water (dotted); the ab initio potential from ref 17 (dashed).

To compare different potentials, the energies of ion−water interactions have been computed as a function of the ion−oxygen distance for the most favorite orientation shown in the insert in Figure 1. The calculations have been performed for the Lennard-Jones parameters from Table 1 and two models of the water molecule (flexible (BJH),[27] E_{flexible}, and rigid (SPC/E),[28] E_{rigid}), and also for the ab initio potentials[17] E_{abin}. For Na^+ the minimal value of E_{flexible} is about 20% higher than the minimum of E_{rigid}. That difference results from higher partial charges of the latter. The lowest energy is seen for E_{abin}.

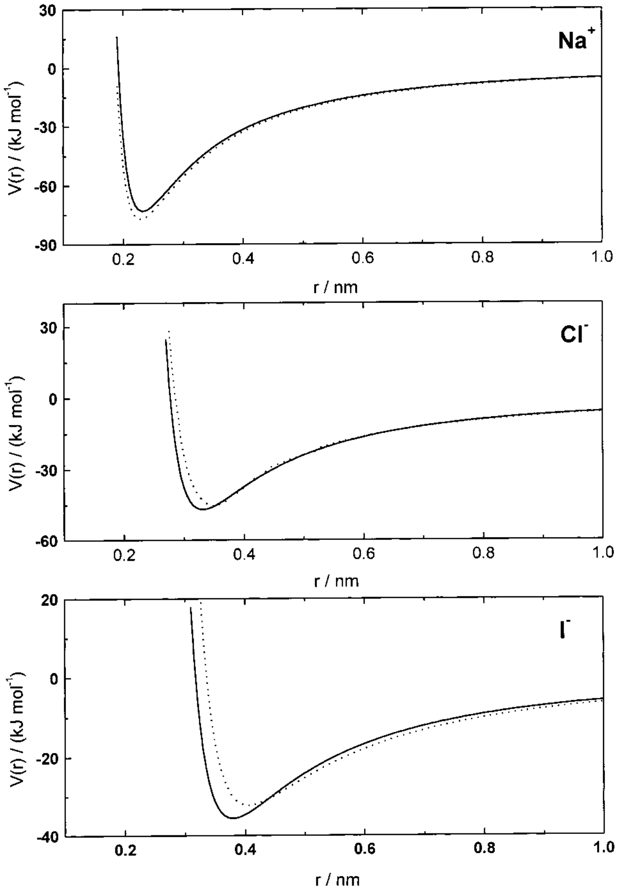

Figure 2. Binding energies of the ion−water (solid lines) and ion−methanol (dashed) complexes versus the ion−oxygen distance calculated for the pair potential parameters from Table 1. Orientations of the solvent molecules are the same as shown in Figure 1.

For $\mathrm{Cl^-}$, the highest energy is found for E_{flexible} and the lowest, about −74 kJ/mol, for E_{rigid}. It is worth emphasizing here that the commonly used SPC/E potential does not reflect differences between the sodium and chloride ions in their interactions with water. The ratio of the minimal energies predicted for these ions by the SPC/E model is about 1.12. The corresponding ratios calculated with the BJH model, 1.5 and 1.75 for the LJ and ab initio potentials, respectively, seem to be more realistic regarding the differences in the enthalpy of hydration of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$.[36]

Interaction energies of $\mathrm{Na^+}$, $\mathrm{Cl^-}$, and $\mathrm{I^-}$ ions with both solvent components are compared in Figure 2. As can be seen, none of the solute−solvent interactions is favored by the assumed potentials. For $\mathrm{Na^+}$ and $\mathrm{Cl^-}$, differences in ion−water and ion−methanol interactions are below 5%. Only for the iodide ion, the energy minimum of the $\mathrm{I^-}$−water complex is about 10% deeper and the position of this minimum is shifted by 0.02 nm toward the ion.

3. Details of the Simulation

MD simulations were carried out for methanol−water solutions of NaCl, NaI, and for fictitious solutions of $\mathrm{Na^0Cl^0}$. All simulations were performed for the standard NVE ensemble. The periodic cubes contained 400 solvent molecules and 16 ions or uncharged spheres. The lengths of the periodic boxes were calculated from the experimental densities of the corresponding NaCl or NaI solutions at 298 K.

The initial configurations were obtained by random placement of particles in the cubic box. Ewald summation was used for Coulomb interactions, and the shifted force potential method was used for all non-Coulomb interactions.[35] The simulation time step was 0.25 fs. After about 15 ps of equilibration, simulation of each system was extended up to 100 ps. Velocities and coordinates of all sites were collected in 1 fs intervals. In all simulations, stability of the total energy was better than 0.01%.

4. Results and Discussion

4.1. Radial Distribution Functions and Spatial Orientation. The nearest surrounding of the solute in a methanol−water mixture can be described by four radial distribution functions: two for water sites ($\mathrm{O_W}$ and $\mathrm{H_W}$) and only two for methanol sites ($\mathrm{O_M}$ and $\mathrm{H_M}$). Examples of radial distribution functions in aqueous and methanol solutions are shown in Figures 3 and 4. Characteristic parameters of all ion−oxygen radial distribution functions are summarized in Table 2. These are positions of the first maximum R_{max}, its height $g_{ij}(R_{\mathrm{max}})$, and a solvation number $n_j(r_{\mathrm{min}})$ calculated by integration up to the first minimum, r_{min}, of $g_{ij}(r)$:

$$n_j = 4\pi\rho_j \int_0^{r_{\mathrm{min}}} g_{ij}(r) r^2\, \mathrm{d}r \qquad (4)$$

where ρ_j is the number density of the *jth* solvent component.

There is also shown methanol mole fraction in the first coordination shell $x_{\mathrm{M}}^{\mathrm{shell}}$ calculated as follows:

$$x_{\mathrm{M}}^{\mathrm{shell}} = \frac{n_{\mathrm{M}}}{n_{\mathrm{M}} + n_{\mathrm{W}}} \qquad (5)$$

In aqueous solutions of NaCl and NaI, the position of the sharp maximum of the cation−oxygen radial distribution functions $g_{\mathrm{Na^+O_W}}$ at $R_{\mathrm{max}} = 0.245 \pm 0.005$ nm is in excellent accord with the distance of 0.24 nm reported from X-ray[37] and neutron diffraction[38] experiments. In methanol solution, the peak of $g_{\mathrm{Na^+O_M}}$ appears at the same distance. Solvent compositions do not affect the peak positions of either $g_{\mathrm{Na^+O_W}}$ or $g_{\mathrm{Na^+O_M}}$ (Table 2). This explains why diffraction experiments cannot answer the question concerning the selective solvation of ions.[39]

First peaks of $g_{\mathrm{Na^+H_W}}$ and $g_{\mathrm{Na^+H_M}}$ are broader and lower. They are shifted to the longer distance by about 0.06 nm, suggesting the antidipole orientation of solvent molecules in the coordination shell of $\mathrm{Na^+}$. The antidipole orientation of either water or methanol neighbors is confirmed by angular distribution functions shown in Figure 5.

A discharging of $\mathrm{Na^+}$ significantly affects the nearest neighborhood. The preferred orientation, observed in the Coulomb field of the cation, disappears for its uncharged counterpart $\mathrm{Na^0}$ (Figure 5), and, within statistical uncertainty, the maxima of $g_{\mathrm{Na^0H_W}}$ and $g_{\mathrm{Na^0H_M}}$ coincide with those of $g_{\mathrm{Na^0O_W}}$ and $g_{\mathrm{Na^0O_M}}$, respectively (Figure 3). First peaks of the $g_{\mathrm{Na^0O_W}}$ and $g_{\mathrm{Na^0O_M}}$ are broader and lower in comparison with those for cation. Positions of the $g_{\mathrm{Na^0O_W}}$ and $g_{\mathrm{Na^0O_M}}$ peaks are independent of solvent composition, similarly as for $\mathrm{Na^+}$, but the distance between $\mathrm{Na^0}$ and the oxygen is about 0.02−0.03 nm longer compared to the $\mathrm{Na^+}$−O separation (Table 2).

In aqueous solution the $\mathrm{Cl^-}$−oxygen and $\mathrm{Cl^-}$−hydrogen radial distribution functions exhibit the first maximum at 0.36 and 0.265 nm, respectively (Figure 4). In methanol solution the positions of the first peaks are the same within the statistical uncertainty (Table 2). Such coincidence is in good agreement with the neutron scattering data.[38,40,41] The $\mathrm{Cl^-}$−O distances of 0.31 and 0.33 nm were reported for aqueous and methanol solutions, respectively, whereas the separation between $\mathrm{Cl^-}$ and hydrogen in these solutions was found to be 0.23 and 0.22 nm,

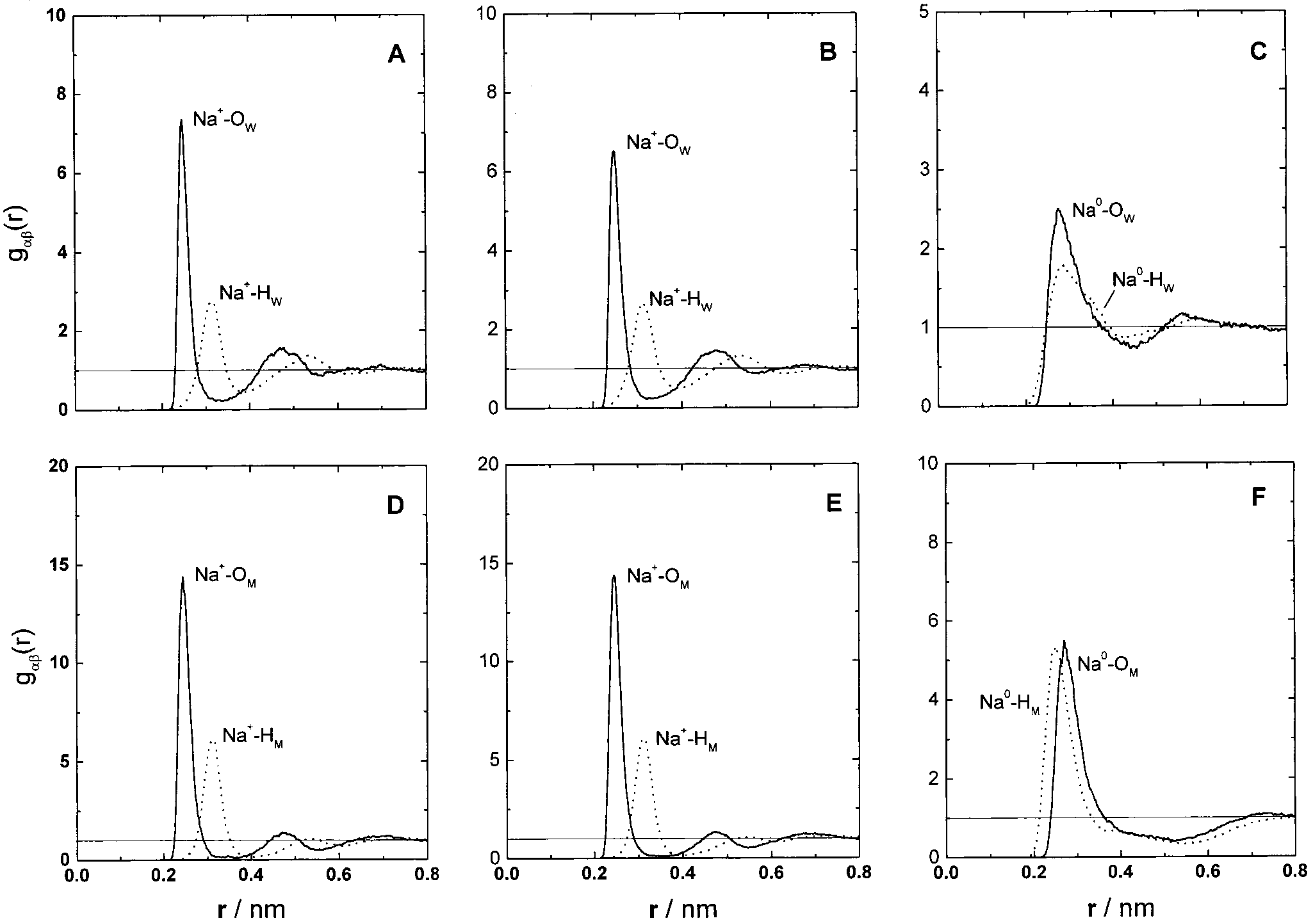

Figure 3. Cation−oxygen (solid), cation−hydrogen (dotted) radial distribution functions in aqueous (upper pannels) and methanol (bottom) solutions of: NaCl (A) and (D), NaI (B) and (E), and Na^0Cl^0 (C) and (F).

respectively. The distance between Cl^-−H is about 0.095 nm shorter. It suggests the OH bond orientation of solvent molecules in the shell. An existence of an almost linear hydrogen bond between Cl^- and its nearest neighbors is evidenced by the distribution functions in Figure 5.

The uncharged sphere Cl^0, contrary to Cl^-, is not able to orient solvent molecules. Thus the peaks of $g_{\mathrm{Cl^0O}}$ and $g_{\mathrm{Cl^0H}}$ functions are broader compared to those for Cl^-. They are separated by only 0.03 nm, suggesting almost random orientation of the solvent molecules in the solvation shell. The peak positions of $g_{\mathrm{Cl^0O}}$ and $g_{\mathrm{Cl^0H}}$ depend on x_{M}, contrary to the composition independent maximum of $g_{\mathrm{Cl^-O}}$ and $g_{\mathrm{Cl^-H}}$ functions (Table 2). The former peaks appear at the similar distance. The broad angular distribution in Figure 5 shows, however, weak preferences of the water molecule orientation. This effect is due to the H-bonded network of the solvent (Figure 5). In methanol solution the angular distribution is slightly different as a consequence of a strong repulsion between Cl^0 and methyl group.

As it might be expected, the radial distribution functions for the iodide ion are significantly different. In aqueous solution first peaks of $g_{\mathrm{I^-O_W}}$ and $g_{\mathrm{I^-H_W}}$ appear at 0.41 ± 0.01 and 0.31 ± 0.01 nm, respectively (Figure 4). A broad maximum of the former function counts about 25 water molecules in the solvation shell of I^- and their positions are not fixed. Although the charge density of I^- is small, such hydration number has not been expected. A similar coordination number has been reported for the tetralkylammonium cation,[42] which acts like a nonpolar solute. The coordination shell of I^- is, however, not like that of $(CH_3)_4N^+$. The shorter I^-−H distance from the anion to hydrogen as compared with the I^-−O separation suggests that some of the water molecules are OH bond oriented toward I^-. The angular distribution in Figure 5 confirms this supposition. Integration of the first peak of $g_{\mathrm{I^-H_W}}$ shows that only three water molecules form hydrogen bonds with the anion. Addition of methanol does not affect the position of the first maximum of $g_{\mathrm{I^-O_W}}$ but changes the height of the peak (Table 2). The lowest peak, observed at $x_M = 0.3$, suggests that in this solution positions of water molecules in the vicinity of the iodide ion are less fixed than in aqueous solution.

An effect of solvent composition on the anion−solvent g functions is more noticeable for methanol neighbors. If methanol concentration exceeds 30 mol %, the single broad peak of $g_{\mathrm{I^-O_M}}$, observed in water-rich solutions, splits into two peaks centered at 0.40 ± 0.01 and 0.51 ± 0.01 nm, respectively. A split of the $g_{\mathrm{I^-H_M}}$ function has been also found, but only in net methanol and methanol-rich solutions. The $g_{\mathrm{I^-H_M}}$ peaks appear at 0.31 ± 0.01 and 0.57 ± 0.01 nm, respectively. The difference of the positions of the first peaks of $\mathrm{g_{I^-O_M}}$ and $g_{\mathrm{I^-H_M}}$ indicates that these methanol molecules prefer OH bond orientation in the field of anion. Integration of the first peaks of $g_{\mathrm{I^-O_M}}$ and $g_{\mathrm{I^-H_M}}$ results in 2−3 molecules forming the H bonds with I^-. This result is in excellent agreement with the solvation number of iodide ions deduced from the self-diffusion measurements.[16] Angular distribution functions in Figure 5 have been calculated for the methanol molecules, represented by two peaks of $g_{\mathrm{I^-O_M}}$, separately. The angular distribution confirms formation of H bonds between I^- and the molecules represented by the first peak of $g_{\mathrm{I^-O_M}}$, whereas eight methanol molecules, represented by the second peak, prefer dipole orientation toward the iodide ion.

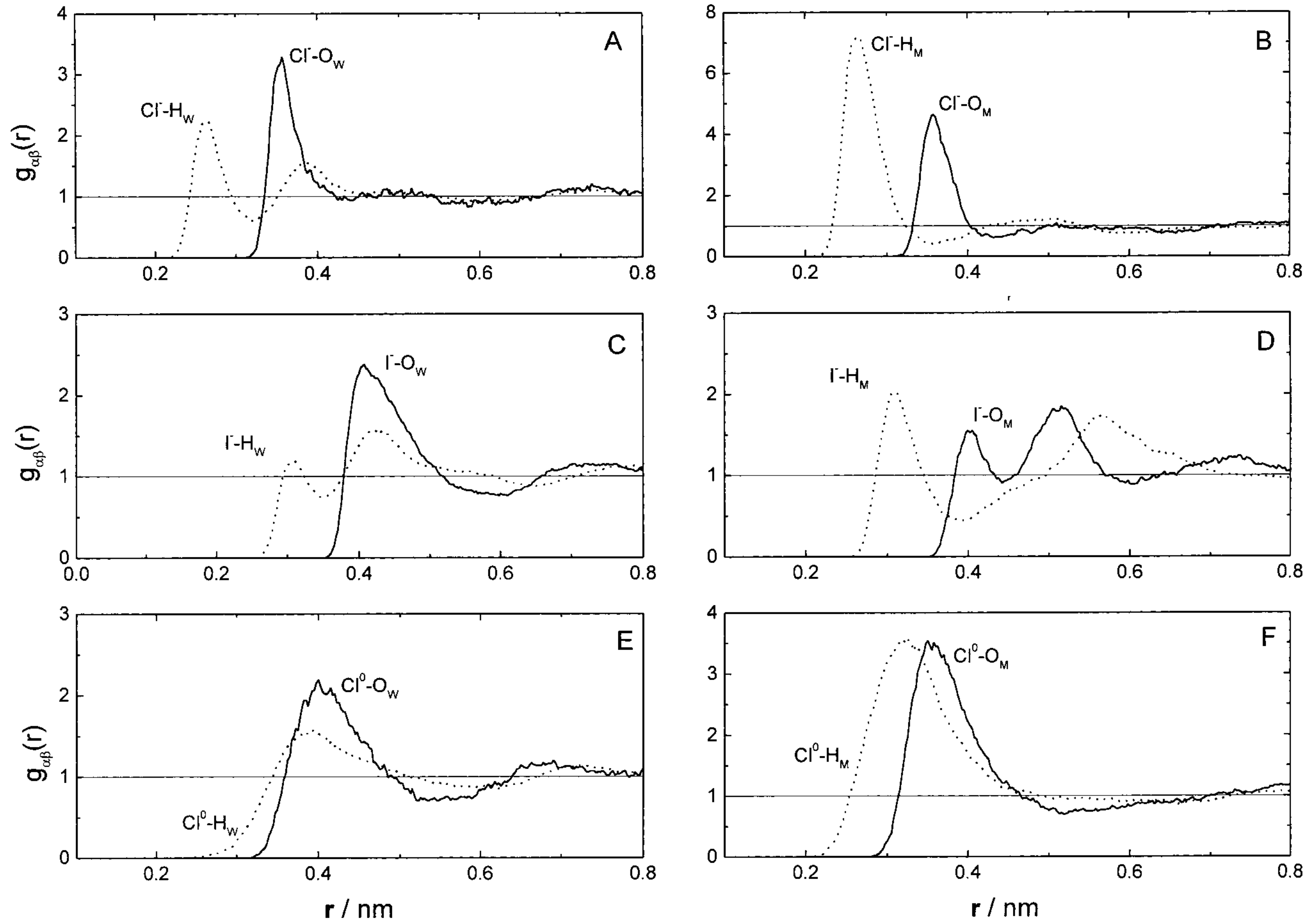

Figure 4. Anion−oxygen (solid), anion−hydrogen (dotted) radial distribution functions in aqueous (left pannels) and methanol (right) solutions of: NaCl (A) and (B), NaI (C) and (D), Na^0Cl^0 (E) and (F).

The methanol−water mixture is a nonideal solvent with nonadditive changes of the molar volume. Thus the methanol mole fraction in the shells of solutes x_M^{shell}, calculated from eq 5 and summarized in Table 2, can differ from the solvent composition x_M, because of nonlinear variations of the number densities.[1] To find out whether selective solvation occurs, the x_M^{shell} values must be compared with the expected methanol mole fraction calculated as[1]

$$x_M(\text{expected}) = \frac{(n_M)^0 \dfrac{\rho_M}{(\rho_M)^0}}{(n_M)^0 \dfrac{\rho_M}{(\rho_M)^0} + (n_W)^0 \dfrac{\rho_W}{(\rho_W)^0}} \qquad (6)$$

where $(n_M)^0$ and $(n_W)^0$ are the solvation numbers of the solute in net solvents, methanol and water, respectively, $(\rho_M)^0$ and ρ_M denote the number densities of methanol in net methanol and methanol−water mixtures, respectively, while $(\rho_W)^0$ and ρ_W are the water number densities in aqueous solution and mixtures, respectively.

The x_M^{shell} values are presented as a function of the expected methanol mole fraction x_M(expected) in Figure 6. As seen the composition of the Na^+ shell, x_M^{shell}, is very close to the expected one. The only exception is the methanol-rich mixture, $x_M = 0.9$, where the x_M^{shell} value is smaller than x_M(expected). It suggests preferential hydration of Na^+, in agreement with the conclusion drawn from the self-diffusion experiments.[16] As seen from Table 2, the same x_M^{shell} values were obtained for NaCl and NaI solutions. It means that the counterion does not affect composition of the cation shell.

Discharging of the cation results in a significant increase of methanol concentration in the shell of Na^0. Although interactions of the uncharged Na^0 sphere with either methanol or water are very similar, the solvation shell contains many more methanol molecules than expected (Figure 6). Thus the uncharged sphere of the same size as Na^+ is preferentially solvated by methanol molecules.

The observed and expected compositions of the nearest neighborhood of counterions are compared in the right part of Figure 6. In methanol−water mixtures the x_M^{shell} values observed for chloride ions exceed noticeably x_M(expected), indicating selective solvation of Cl^- by methanol molecules. Such preference is not observed for the discharged anion. Even though concentration of methanol in the coordination shells of Cl^0 is higher than in the solvent (Table 2), x_M^{shell} fits the methanol mole fraction expected for that nonideal mixture. It means that selective solvation of the uncharged sphere of a similar size as the chloride anion does not occur.

Methanol content in the vicinity of iodide ions was calculated for all neighbors and, separately, for the H-bonded molecules. The x_M^{shell} values in Table 2 show that in both cases methanol concentration in the vicinity of iodide ions is higher than in the solvent.

If all neighbors of I^- are considered, the comparison of x_M^{shell} and x_M(expected) shows the selective solvation by methanol. This preference seems to disappear for the H-bonded molecules. However, a careful inspection of Table 2 shows that in the mixed

TABLE 2: Characteristic Parameters of the Solute−Oxygen Radial Distribution Functions[a]

x_M	solute	$R_{max}(i-O_W)$/nm	$g_{iOW}(R_{max})$	n_W	$R_{max}(i-O_M)$/nm	$g_{iOm}(R_{max})$	n_M	x_M^{shell}
0.0	Na^+ [b]	0.247 *(0.230)*	7.36 *(8.61)*	6.08 *(6.11)*				0
	Na^+ [c]	0.250	6.51	5.92				0
	Na^0	0.275	2.51	10.24				0
	Cl^-	0.357*(0.330)*	3.21*(3.14)*	12.25 *(8.68)*				0
	I^-	0.407	2.38	24.65				0
	Cl^0	0.400	2.22	18.23				0
0.1	Na^+ [b]	0.247 *(0.230)*	7.02 *(8.54)*	4.80 *(4.76)*	0.245 *(0.237)*	14.42 *(15.46)*	1.23 *(1.25)*	0.20 *(0.21)*
	Na^+ [c]	0.247	6.13	4.44	0.245	15.67	1.24	0.21
	Na^0	0.262	1.92	4.58	0.272	8.56	2.60	0.36
	Cl^-	0.355 *(0.337)*	2.59 *(2.23)*	7.66 *(5.80)*	0.352 *(0.325)*	10.48*(14.09)*	2.76*(2.25)*	0.26 *(0.28)*
	I^-	0.400	2.00	20.3	0.472	3.41	3.87	0.17
	Cl^0	0.392	1.95	12.8	0.352	4.58	2.77	0.18
0.3	Na^+ [c]	0.247	4.68	2.23	0.245	13.03	2.39	0.52
	I^-	0.405	1.31	8.15	0.485	2.76	8.24	0.50
0.5	Na^+ [b]	0.247 *(0.230)*	8.88 *(11.20)*	2.51*(2.61)*	0.242*(0.235)*	12.80 *(13.75)*	3.14*(3.30)*	0.56 *(0.56)*
	Na^+ [c]	0.247	9.12	2.47	0.245	12.20	3.07	0.55
	Na^0	0.260	1.55	1.07	0.277	5.89	5.31	0.83
	Cl^-	0.360	1.73	1.07 *(0.52)*	0.355 *(0.325)*	7.15 *(12.04)*	6.51 *(6.65)*	0.86 *(0.93)*
	I^- [d]	0.412	1.83	5.53	0.395; 0.495	2.91; 1.93	2.20; 9.60	−; 0.64
	Cl^0	0.405	2.18	5.59	0.360	3.62	7.43	0.57
0.9	Na^+ [b]	0.245 *(0.230)*	19.28 *(24.19)*	0.75 *(0.80)*	0.245 *(0.235)*	12.00 *(13.72)*	4.36*(4.90)*	0.85 *(0.86)*
	Na^+ [c]	0.247	16.17	0.72	0.245	11.81	4.10	0.85
	Na^0	0.262	2.35	0.31	0.265	5.17	5.72	0.95
	Cl^-	0.375	1.19	0.24	0.352 *(0.325)*	4.59 *(8.84)*	6.74 *(7.22)*	0.97 *(1.00)*
	I^-	0.407	2.03	0.96	0.411; 0.513	1.77; 1.74	2.62; 11.16	−; 0.92
	Cl^0	0.390	3.35	1.36	0.390	3.35	10.08	0.88
0.1	Na^+ [b]				0.245 *(0.232)*	14.40 *(17.77)*	5.53*(6.02)*	1
	Na^+ [c]				0.245	14.39	5.52	1
	Na^0				0.270	5.30	6.41	1
	Cl^-				0.357 *(0.330)*	4.63 *(7.40)*	6.25 *(7.22)*	1
	I^-				0.400; 0.515	1.77; 1.74	2.61; 11.06	1
	Cl^0				3.70	3.31	10.86	1

[a] R_{max} denotes the distance, where radial distribution function has a maximum of the height $g_{ij}(R_{max})$, n_j is a solvation number, and x_M^{shell} is methanol mole fraction in the first coordination shell. [b] In NaCl solutions. Results for the same system from simulations with the ab initio potentials[17,18] extended up to 100 ps are given in parentheses. [c] In NaI solutions. [d] For split peaks parameters of both are given.

solvents, even for $x_M < 0.5$, only methanol molecules are H-bonded with iodide ions.

The results discussed above suggest that in highly associated solvents the solvation of solutes is determined by interactions between solvent molecules. A tendency to preserve the H-bonded network is decisive for the composition of the solute neighborhood. Ab initio calculations[13] and results of MD simulations[8] indicate that the H bond formed between the H donor water and the H acceptor methanol molecules is energetically more favorable. In consequence of that, preferential hydration of Na^+ and selective solvation of the anions is observed. Antidipole orientation of solvent molecules in the cation field favors water molecules acting as the H donors, whereas the OH bond orientation in the anion field agrees with the preferences shown by the methanol molecule. The quantitative studies show that the influence of sodium halides on the H bonded network of the solvent is limited to the first coordination shells of ions.[8,9]

Differences in solvation of Na^0 and Cl^0 confirm the hypothesis that preservation of the H bonded network is decisive. In consequence of different sizes of these neutral solutes, their influence on the structure of water and of methanol is different. As seen from Figure 5 the orientation of water and methanol molecules around Cl^0 is very similar, and a lack of any preferences is observed in mixed solvents. Completely random arrangement of methanol molecules in the surrounding of Na^0 contrasts with some preferences observed for Na^0 in aqueous solution. In consequence, in mixed solvents water molecules avoid the vicinity of Na^0.

One of the main questions we would like to answer in this paper is to what extent the structure and composition of the coordination shells of Na^+ and Cl^- depend on ion−solvent potentials employed in MD simulation. The outcome of the present work has been set against the results reported previously[1,8,17−19] for the ab initio ion−solvent potentials. The corresponding parameters of the ion−oxygen radial distribution functions are given in parentheses (Table 2).

The LJ-type potentials exhibit noticeably higher binding energies compared to those calculated with the ab initio potentials (Figure 1). Despite this, g_{Na^+O} does not show significant differences. Small changes can be noticed for the peak positions R_{max} and their heights $g(R_{max})$. The shell size r_{min}, solvation numbers $n(r_{min})$, and, in consequence, the composition of solvation shells x_M^{shell} depend slightly on the ion−solvent potential. Both types of Na^+−solvent potentials well reproduced experimental data on the cation−oxygen separation in aqueous and methanol solutions.[38,40] The observed decrease of $g(R_{max})$ might be expected because of the lower binding energies shown by the LJ-type potentials.

In the case of chloride ions, differences in radial distribution functions are more significant. They appear not only in R_{max} and $g(R_{max})$ but also in the shell size and solvation number n_j. The ab initio potentials predict shorter, by about 0.02−0.03 nm, distance between Cl^- and the oxygen. This shorter distance is in better accord with the experimental data.[38−41] In aqueous solution, the broad first peak of g_{Cl^-O} is noticeably worse pronounced compared to that obtained with the ab initio potentials.[17] The running integration number shows no plateau, and estimation of a hydration number is rather ambiguous. The resulting $n_W = 12.3$ is overestimated compared to the ab initio result 8.7[17] as well as to the neutron scattering data reported for the oxygen, 7.0.[38] A more accurate hydration number can

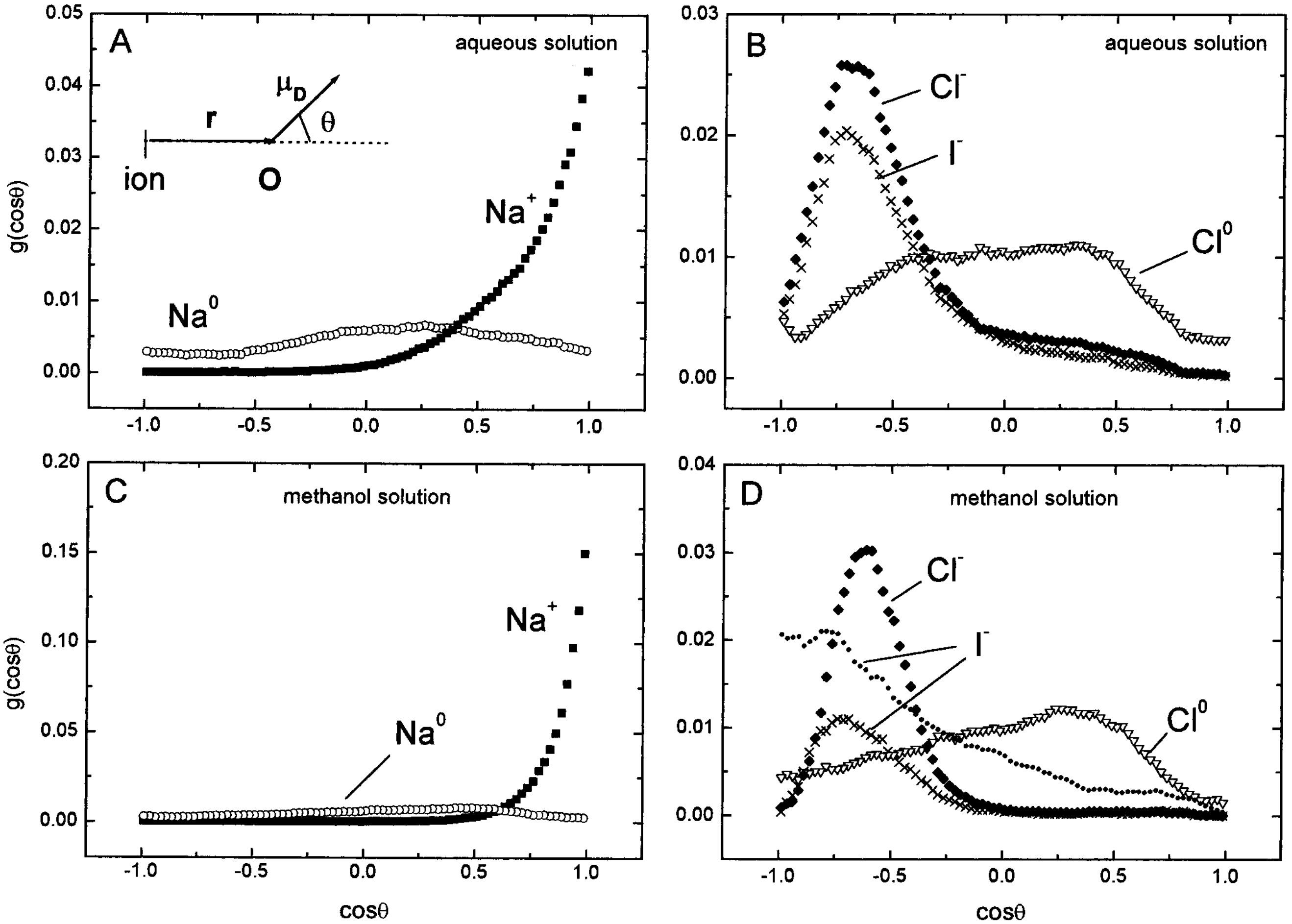

Figure 5. Distribution functions of angular orientation of the nearest neighbors of Na$^+$ (■), Na^0 (○), Cl$^-$ (◆), Cl^0 (▽), I$^-$ H-bonded (×) and all (....) neighbors (see text), in aqueous (A,B) and methanol (C,D) solutions. The angle θ defined in the inset.

be estimated from the better-pronounced Cl$^-$−H$_W$ peak. Integration of this peak leads to $n_W = 7$, in quite good accord with the neutron scattering data for the hydrogen 6.4.[38] In methanol solution the solvation number $n_M \sim 6-7$ for both types of the potentials is in good agreement with the experimental value $n_M \sim 6$.[41] The LJ-type potentials[20−25] are known to neglect non-Coulomb interaction between an ion and the hydroxyl hydrogen. Much better accord with experiment obtained for the methanol solution indicates that neglect of these terms is less important in methanol than in aqueous systems for which the ab initio potentials[17] occur to be more adequate.

Despite differences in the solvation numbers calculated for both types of Cl$^-$−solvent potentials, the $x_M^{\rm shell}$ values listed in Table 2 are very close and show that the chloride ion is selectively solvated by methanol molecules (Figure 6).

4.2. Residence Time of Solvent Molecules in the Coordination Shells. A residence time of solvent molecules in the coordination shell of a solute provides information on whether the solute and its shell can be considered as a molecular aggregate. The residence time has been calculated from the time correlation function $R(t)$, defined by Koneshan et al.:[23]

$$R(t) = \frac{1}{n_{\rm solute} n_S} \sum_{i=1}^{n_{\rm solute}} \sum_{j=1}^{n_S} \theta_{ij}(0)\, \theta_{ij}(t) \qquad (7)$$

where $n_{\rm solute}$ is the number of solutes and n_S denotes the number of solvent molecules in the first shell. $\theta_{ij}(t)$ is the step function equal to 1 if the jth solvent molecule lies within the first coordination shell of the ith solute, and zero otherwise. According to that definition, $R(t)$ represents a fraction of the molecules staying within coordination shells after time t has elapsed. Starting from a given configuration the $\theta_{ij}(t)$ functions have been calculated with time interval Δt. Thus the solvent molecule is allowed to stay outside the shell for a period shorter than Δt. The calculations have been performed with various time intervals $0.1 \leq \Delta t \leq 0.5$ ps, and we did not find any noticeable influence of Δt on the resulting $R(t)$ function. All $R(t)$ functions have been fitted to a second-order exponential decay:

$$R(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_S}\right) \qquad (8)$$

The first term in eq 8 describes escape of solvent molecules located close to a border of the shell. This process is rather fast with the characteristic time $\tau_1 < 1$ ps. The second term reflects a persistence of the shell characterized by the residence time of solvent molecules τ_S. The parameters A_1 and A_2 represent percentages of molecules involved in the processes described above.

Separate calculations of $R(t)$ functions have been performed for water and methanol neighbors, and the obtained residence times τ_W and τ_M are summarized in Table 3. For comparison, the residence times obtained with the ab initio potentials[1] are shown in parentheses.

In aqueous solutions about 85% of water molecules persist in the coordination shell of Na$^+$ during about 19 ps. This value is comparable with the results reported in the literature 17.5,[23]

TABLE 3: Fitting Parameters for the Second-Order Exponential Decay of the $R(t)$ Functions (eq 8) Describing the Residence of Solvent Molecules in the Coordination Shells of Charged and Discharged Ions[a]

solvent	x_M	A_2			τ_s/p		
water		**Na^+ (NaCl)**	**Na^+ (NaI)**	**Na^0**	**Na^+ (NaCl)**	**Na^+ (NaI)**	**Na^0**
	0.0	0.86 *(0.88)*	0.85	0.78	19.4 ± 0.4 *(173.0 ± 0.8)*	18.9 ± 0.5	2.0 ± 0.4
	0.1	0.86 *(0.94)*	0.86	0.66	18.1 ± 0.6 *(86.0± 0.5)*	17.2 ± 0.5	2.4 ± 0.4
	0.3	−	0.79	−	−	10.1 ± 0.3	−
	0.5	0.81 *(0.75)*	0.81	0.61	16.9 ± 0.6 *(15.0 ± 0.4)*	15.9 ± 0.5	2.7 ± 0.5
	0.9	0.85 *(0.94)*	0.83	0.84	27.0 ± 0.6 *(44.0 ± 0.5)*	26.9 ± 0.6	5.4 ± 0.5
methanol		**Na^+ (NaCl)**	**Na^+ (NaI)**	**Na^0**	**Na^+ (NaCl)**	**Na^+ (NaI)**	**Na^0**
	0.1	0.87 *(0.98)*	0.88	0.88	14.3 ± 0.7 *(>150)*	12.3 ± 0.6	7.3 ± 0.5
	0.3	−	0.88	−	−	13.2 ± 0.8	−
	0.5	0.70 *(0.75)*	0.66	0.50	16.9 ± 0.4 *(15.0 ± 0.5)*	16.5 ± 0.5	18 ± 1
	0.9	0.90 *(0.93)*	0.91	0.82	14.3 ± 0.5 *(45.0 ± 0.5)*	13.8 ± 0.6	5.4 ± 0.5
	1.0	0.92 *(0.92)*	0.92	0.65	14.5 ± 0.3 *(45.0 ± 0.4)*	13.1 ± 0.5	5.3 ± 0.5
water		**Cl^-**	**I^-**	**Cl^0**	**Cl^-**	**I^-**	**Cl^0**
	0.0	0.75 *(0.76)*	0.65	0.76	13.0 ± 0.8 *(19.5 ± 0.3)*	11.0 ± 0.5	2.0 ± 0.6
	0.1	0.73 *(0.76)*	0.64	0.39	9.8 ± 0.9 *(14.5 ± 0.9)*	7.8 ± 0.6	3.9 ± 0.5
	0.3	−	0.65	−	−	7.3 ± 0.3	−
	0.5	0.40 *(0.33)*	0.53	0.68	5 ± 1 *(8 ± 1)*	6.5 ± 0.5	3.9 ± 0.7
	0.9	0.35	0.53	0.62	2 ± 1	5 ± 1	4.1 ± 0.7
methanol		**Cl^-**	**I^- [b]**	**Cl^0**	**Cl^-**	**I^- [b]**	**Cl^0**
	0.1	0.85 *(0.87)*	0.81	0.73	14.4 ± 0.7 *(30 ± 1)*	12.4 ± 0.8	5.6 ± 0.5
	0.3	−	0.80	−	−	13.9 ± 0.6	−
	0.5	0.85 *(0.87)*	0.98 *0.58*	0.56	14.9 ± 0.8 *(29.9 ± 0.8)*	25.1 ± 0.3 5.1 ± 0.5	5.9 ± 0.5
	0.9	0.88 *(0.89)*	0.98 *0.59*	0.71	13.3 ± 0.6 *(20.1 ± 0.5)*	25.8 ± 0.8 6.0 ± 0.9	5.4 ± 0.6
	1.0	0.85 *(0.84)*	0.98 *0.63*	0.78	17.9 ± 0.4 *(21.9 ± 0.4)*	26.1 ± 0.5 6.4 ± 0.7	5.4 ± 0.5

[a] Results from the simulations with the ab initio potentials[1] are given in parentheses. [b] Parameters for the H-bonded molecules and for those represented by the second peak of the $g_{I^-O_W}$ (see text) are given in upper and lower row, respectively.

14.7,[43] and 9.9 ps,[44] which have been obtained assuming the LJ-type potentials for Na^+. Models of water molecules were, however, different: SPC/E[23,43] and MCY,[44] respectively. The values of τ_W do not show any correlation with the strength of ion−water interactions. The shortest time, 9.9 ps, was reported for the MCY water model, exhibiting the lowest binding energy of the Na^+-H_2O complex.

One should notice that the water residence time of 173 ps obtained with the ab initio potential for Na^+-H_2O interactions was 1 order of magnitude longer.[1] It is difficult to decide which of the model potentials correctly reproduces the residence time, because direct comparison with the experimental data is not possible. An exchange of solvent molecules between the coordination shell and the bulk solvent could be investigated by tracer techniques. The exchange rates are known only for a few ions of high charge density. For Cr^{3+} the exchange rate in aqueous solutions, about 8×10^{-7} s^{-1}, was reported.[45,46] Such low rate of exchange means that water molecules persist several hours in the hydration shell of Cr^{3+}. Even taking into account that the charge density of Cr^{3+} is about 1 order of magnitude higher compared to that of Na^+, water residence time in the Na^+ hydration shell of about 20 ps seems to be unrealistic.

An indirect verification of residence times can be obtained from the experimental data on self-diffusion coefficients of the ions. The residence time can be compared with the characteristic time of ion translation resulting from the Einstein formula:

$$(\tau_{\mathrm{ion}})_{\mathrm{T}} = \frac{l^2}{6D_{\mathrm{ion}}} \tag{9}$$

where the average hopping distance l is usually considered as the limit of the first coordination shell. If the residence time noticeably exceeds $(\tau_{\mathrm{ion}})_{\mathrm{T}}$, the ion and its shell are considered as a molecular aggregate. In that case the hydrodynamic radius is significantly greater than in the crystal. Self-diffusion coefficients of Na^+ were measured at 298 K in solutions of NaCl and NaI for the same solute concentration as in the simulated systems.[3,4] The D coefficient of Na^+ decreases from 1.2×10^{-9} m^2 s^{-1} to 0.85×10^{-9} m^2 s^{-1} in 1.1 M aqueous and 0.55 M methanol solution, respectively. Substituting these values in eq 9 and assuming l equal to the shell size 0.32 nm, one obtains $(\tau_{Na^+})_T \approx 20$ ps. The hydrodynamic radius of Na^+, derived from the diffusion data, significantly exceeds its crystallographic radius in aqueous solution and over the whole range of methanol−water mixture composition.[16] It suggests that the residence time of solvent molecules in the Na^+ shell must be noticeably longer than 20 ps. Thus the ab initio potential seems to predict more reasonable lifetime of the Na^+ shell.

As seen from Table 3, the residence times of water molecules in Na^+ shells in solutions of NaCl and NaI are the same within

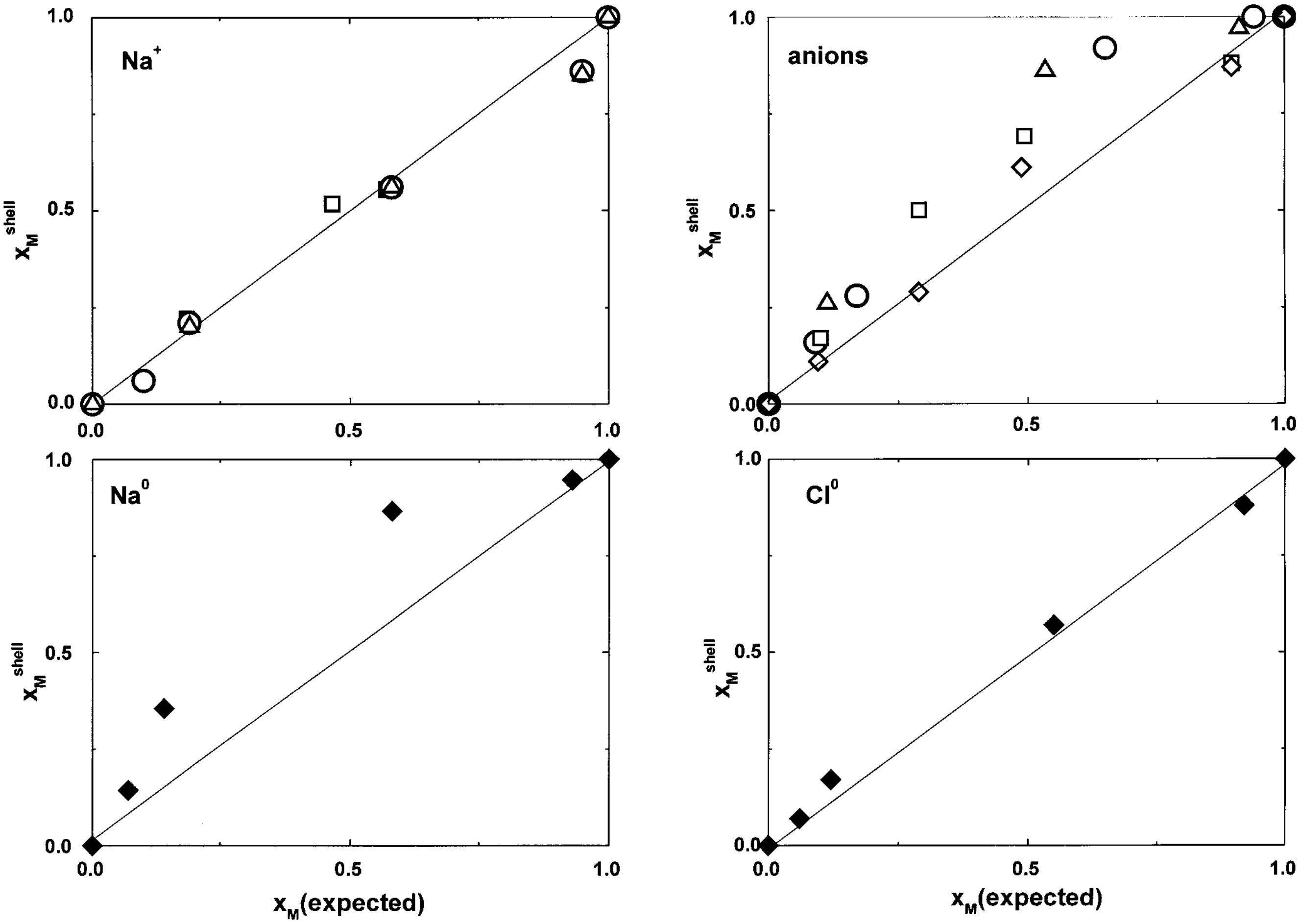

Figure 6. The methanol mole fraction x_M^{shell} from eq 5 versus the expected composition x_M(expected) calculated from eq 6. Ions in solutions of: NaCl (△), NaCl from ref 1 (○), Na^{0}Cl^0 (◆), NaI (□,◇) (see text).

the statistical uncertainty. The counterion does not affect the lifetime of the cation coordination shell. Addition of methanol slightly influences the τ_W value. The shortest time is seen at $x_M = 0.3$. Such behavior agrees well with the observed variation of the hydrodynamic radius of Na$^+$ in methanol−water solutions. It has been shown that addition of methanol reduces the hydrodynamic radius, and the smallest radius was found at $x_M = 0.3$.[16] Increase of τ_W in methanol-rich solvent, where selective hydration of Na$^+$ occurs, indicates the existence of long-living aggregates, evidenced by the same self-diffusion coefficients of Na$^+$ and water.[3,4]

Residence time of methanol molecules in the Na$^+$ shell is not affected by the counterion. Its value of about 14 ps is lower than τ_W and almost independent of the solvent composition. In methanol solution τ_M is shorter than $(\tau_{Na^+})_T$. The τ_M(ab initio) value of 45 ps seems to be more realistic, because in methanol solution the hydrodynamic radius of Na$^+$ is significantly greater than its crystallographic radius.[16]

In aqueous solution, the lifetime of the Cl$^-$ hydration shell, of about 13 ps, is shorter than reported for the LJ-type Cl$^-$ potential and SPC/E water (17.5 ps[23]), but longer than the 4.5 ps calculated for MCY model.[44] Similarly as for Na$^+$, the longest residence time, about 19 ps, was found with the ab initio potential,[1] whereas the lowest binding energy of the Cl$^-$−H$_2$O complex was obtained for the MCY water model. Thus there is no relation between persistence of the Cl$^-$ shell in aqueous solution and the strength of ion−water interactions. The residence time of water molecules in the shells of Cl$^-$ and I$^-$ is similar and decreases with increasing methanol concentration. As seen from Table 3, the computed τ_W values reported for Cl$^-$ and I$^-$ are slightly shorter than that for Na$^+$.

To estimate characteristic time of anion translation 0.45 and 0.57 nm was assumed as the hopping distance of Cl$^-$ and I$^-$, respectively. The anionic self-diffusion coefficients are very close and decrease from 1.95×10^{-9} m^2 s^{-1} to 1.45×10^{-9} m^2 s^{-1} in 1.1 M aqueous and 0.55 M methanol solution, respectively.[3,4] With these values eq 9 yields the characteristic time $(\tau_{Cl^-})_T \approx 20$ ps. Slightly shorter lifetime of the hydration shells is consistent with the self-diffusion measurements.[16] They showed that the hydrodynamic radii of Cl$^-$ and I$^-$ are noticeably greater than their crystallographic radii only for $x_M > 0.5$. According to this picture the methanol residence time in the shell of Cl$^-$ is too short.

Residence time of methanol molecules in the neighborhood of I$^-$ in methanol-rich solvent has been described by two sets of parameters corresponding to the persistence of the molecules represented by two peaks of $g_{I^-O_M}$. All H-bonded molecules, represented by the first peak, stay about 26 ps in the vicinity of the iodide ion, and their residence time is independent of x_M. The residence time of the methanol molecules represented by the second peak is short, about 6 ps, and is close to the residence time of methanol in the coordination shells of water molecules.[1] There is also a fast exchange with the bulk solvent, because more than 40% of nonbonded neighbors escape the anion vicinity within 1 ps.

As can be seen from Table 3, the solvation shells of uncharged spheres are unstable. In aqueous solution the residence time of water molecules in the shells of Na^0 and Cl^0 decreases up to 2 ps and is shorter than the lifetime of water pentamers, about 6 ps.[1] Addition of methanol does not noticeably affect the τ_W values.

The residence time of methanol molecules in the shell of Na^0 and Cl^0, of 6 ps, is longer than τ_W and comparable with the lifetime found for methanol neighbors in the vicinity of water molecules.[1] The exception is the equimolar solution, where the solvation shell of Na^0 contains particularly more methanol than expected (Figure 6). At $x_M = 0.5$, $\tau_M \approx 18$ ps is very close to the residence time of methanol in the surrounding of other methanol molecules.[1]

Conclusions

This work improves our understanding of a nature of selective solvation in methanol−water mixtures. In these systems selective solvation is observed, despite very similar interactions of solutes with both solvent components. Comparison of the preferences shown by the solutes of different charge density leads to the conclusion that in highly associated solvents solute−solvent interactions compete with a tendency to preserve the H-bonded network.

Anions are selectively solvated by methanol molecules, but these preferences decrease with decreasing charge density and vanish for the uncharged Cl^0. The preferences exhibited by the anions contrast with those observed for Na^+ and Na^0. The cation shows preferential hydration only in water-deficit solution, whereas its uncharged counterpart is selectively solvated by methanol over the whole range of solvent composition. These opposite preferences result from different orientation of the solvent molecules in the ionic shells and the strength of H-bonds between methanol and water molecules. Ab initio calculations have shown that in the gas phase the H bond between the H acceptor methanol and the H donor water molecules is energetically favorable.[13] Solvent molecules in the shells of Na^+ exhibit the antidipole orientation. That they may act only as the H donors is what discriminates methanol molecules. The OH bond orientation toward the anion favors methanol molecules, which prefer to be the H acceptors.

Our simulations have also shown that structural properties of the solution, described by the characteristic parameters of radial distribution functions, depend slightly on the employed ion−solvent potentials. The type of these potentials has negligible effect on the preferences in Na^+ and Cl^- solvation.

The residence time of solvent molecules in the solvation shell seems to be more sensitive on the type of ion−solvent potential. A comparison of the calculated persistence of solvation shells with the results of self-diffusion measurements leads to the conclusion that the Lennard-Jones potentials underestimate the lifetime of ionic shells. This effect is particularly significant for the Na^+ shell in aqueous and water-rich solutions and probably results from neglect of non-Coulomb interactions of ions with hydrogen atoms.

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