MD Simulation of the Ion Solvation in Methanol-Water Mixtures

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1. Introduction

Sodium, calcium and magnesium ions are essential for the biological activity of many polyelectrolytes. This activity depends on a condensation of the metal ions. There are several clues, which suggest that interactions between the polyelectrolyte and metal ions depend on a hydration of the ion. This accounts for the great interest in the hydration of metal ions, particularly in the systems containing hydrophobic groups. In aqueous solutions the hydration of Na^+, Mg^{2+} and Ca^{2+} differs. The first hydration shells of Na^+ and Mg^{2+} consists of six water molecules and have octahedral symmetry (Dietz et al, 1982; Hawlicka & Swiatla-Wojcik, 1995). The first shell of Ca^{2+} is larger; it contains eight or more water molecules and does not show any regularity (Owczarek et al., 2007). X-ray diffraction studies (Tamura et al., 1992, Megyes et al., 2004) have suggested that all these cations are six-coordinated in methanolic solutions thus their shells are octahedral.

Various experimental techniques can be employed to gain insight into a coordination shell of the ion, but a lack of theory renders even a term 'preferential solvation' misleading. The concept of the preferential solvation has been introduced to explain non-linear changes of solution properties, but now this term is commonly used to emphasise a difference of the compositions of the coordination shell and the bulk solvent. Preferential solvation is usually expected if the ion interacts stronger with one of the solvent components. There are however experimental clues that the selective solvation might be due to a microheterogeneity of the binary solvent.

Methanol-water mixture is a suitable model to study structural aspects of solvation in binary systems, particularly when hydrophobic effects may occur. Both net components are highly associated liquids, but their hydrogen-bonded networks are inconsistent. Water molecules form a 3-dimensional, tetrahedrally coordinated structure, where cavities are filled with monomers (Soper & Phillips, 1986). Extension of the hydrogen bonds over 1 nm causes that liquid water, even at room temperature, behaves like a gel (Dore et al., 2000). Hydrogen-bonded molecules of methanol form zig-zag polymer chains (Narten & Habenschuss, 1984). Though in binary mixture the molecules of methanol and water may form a common hydrogen-bonded network the bulky methyl group causes that methanol molecule cannot simply replace the water molecule in the tetrahedral structure. In consequence the methanol-water mixture may become heterogeneous on the molecular level. Neutron diffraction (Dughan et al., 2004) and X-ray spectroscopy (Guo et al. 2004)

have confirmed that supposition. Despite apparent miscibility of both components, methanol and water clusters are observed over whole concentration range. At particular concentration, near 25-27 mol% of methanol, where transport and thermodynamic properties exhibit extrema, water and methanol form separate, percolating structures (Dughan et al. 2004).

Several experimental techniques were employed to investigate solvation of ions in methanol-water mixtures. Results are, however, inconsistent and lead to contradict conclusions. Therefore both a preferential hydration (Convington & Dunn, 1989; Hawlicka, 1995), as well as a lack of preferences (Holtz et al., 1977) have been postulated for alkali and halide ions in methanol-water mixtures. Though X-ray and neutron scattering measurements should provide a direct insight into the ion coordination shell, their results cannot be decisive for methanol-water mixture, because distances between these ions and the oxygens of either water (Neilson & Enderby, 1979; Licheri et al, 1975) or methanol (Megyes, 2004) are almost the same. Moreover a direct correlation between the alkali earth cations and the methyl group is lacking (Radnai et al., 1995). In such case the scattering techniques are not enough sensitive to investigate the preferential solvation in methanol-water mixture. Thus a molecular dynamics simulation seems to be a useful tool to provide additional information concerning the structure of the ion shell.

A quality of the simulation results depends on the methods used to describe all interactions in the solutions. *Ab initio* quantum mechanics would be the most accurate method, but its application to systems containing ions and a few hundred water molecules could not be expected for the near future. Therefore QM/MM MD simulation seems to be an elegant approach for investigating the aqueous solutions of electrolytes. The ion and its nearest water molecules are treated quantum mechanically. Such approach includes many-body interactions between particles within the solvation shell. QM/MM MD simulations were carried out for aqueous solutions of various ions (Tongraar & Rode, 2003, Rode et al., 2004, Öhrn & Karlström, 2004; Tongraar & Rode, 2005, Payaka et al., 2009; Tongraar et al., 2010). Their results evidenced a significant role of the many-body interactions on structural and dynamical properties of the hydrated ions. These simulations concerned, however, the systems, which contain only one ion, either cation or anion, and a few water molecules. Thus this technique is useless for studies more concentrated solutions, where an association of the ions occurs. The formation of the various types of the ionic pairs, solvent separated, solvent shared and contact pairs, is frequently observed in binary solvents. This phenomenon may affect significantly the solvation of ions.

Classical MD simulations are usually carried out for NVE or NVT ensembles. The volume is fixed and it depends on a number of the particles, temperature, composition of the system. Particles are placed into a periodic cube. The size of the periodic box results from the experimental density of the simulated system. Initial coordinates of particles are frequently chosen from the crystal lattice (Heyes, 1998), however the random distribution of the particles in the cube is better, because it reduces a time of equilibration.

In classical simulations the interactions between molecules are represented by a sum of the pair potentials and many-body interactions are neglected. Usually the pair potential consists of Coulomb term, for which the Ewald summation is applied, and of short-range parts, for which shifted-force potential method (Allen & Tidesly, 1987) is used.

2. Effective pair potentials

Several potentials have been proposed to describe the interaction of the water molecules, but this molecule still remains 'a challenge to model, because it is polar, polarizable, has light H atoms and is flexible' (Heyes, 1998). Only a few of the models consider the water molecule as a flexible body and permit internal vibrations. Most of them are a modification of the simple point charge potential of Berendsen *(*Berendsen et al., 1981*)* They use a potential of the spectroscopic type (Zhu & Wong, 1993; Ferguson, 1995) to describe an intramolecular interaction. Unfortunately SPC model neglects non-Coulomb interactions of hydrogen atoms, which seem to be important in hydrogen-bonded systems.

In simulations presented here the interactions of the water molecules has been described by the BJH potential (Bopp et al., 1983; Jancso & Bopp, 1983) which treats the intermolecular interactions of oxygens and hydrogens by mean of the central force model (CF) (Stillinger & Rahman, 1978) and uses a three body description of intermolecular interactions. This model has been frequently employed to simulate aqueous solutions of electrolytes, both in classical (Dietz et al., 1982; Jancso et al. 1985; Probst et al., 1985, Probst et al., 1991; Hawlicka & Swiatla-Wojcik, 1995, Lavenstein et al. 2000; Ibuki & Bopp, 2009) and in QM/MM MD (Tongraar & Rode, 2003, Rode et al., 2004, Öhrn & Karlström, 2004; Tongraar & Rode, 2005, Payaka et al., 2009; Tongraar et al., 2010) simulations. The BJH potential is appropriate to simulate the methanol-water mixtures, because it is fully consistent with the PHH flexible model (Palinkas et al. 1987) of the methanol molecule. The BJH and PHH, potentials reproduce properly the structure, energies and dynamic properties of the methanol-water mixtures (Palinkas et al., 1991a; Palinkas et al., 1991a, Hawlicka & Swiatla-Wojcik, 2000). An advantage of the flexible models is, that they permit a distortion of the solvent molecules from their equilibrium geometry. In consequence a molecular polarizability is incorporated.

The BJH and PHH potentials consist of two parts, which describe the inter- and intramolecular interactions respectively:

$$V(\rho_i, r_{\alpha\beta}) = V^{\text{intra}}(\rho_i) + V^{\text{inter}}(r_{\alpha\beta}) \tag{1}$$

The intermolecular parts are the sum of Coulombic and non-Coulombic terms. The Coulombic terms result from the partial charges of the interacting sites. In water molecule the partial charges are located on oxygen (-0.66 e) and hydrogen (+0.33 e) atoms. Methanol molecule 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-Coulombic intermolecular O-O, O-H and H-H interactions of the water and methanol molecules are the same as in CF2 model for water (Stillinger & Rahman, 1978) The non-Coulomb interaction of the methyl group with the hydroxyl hydrogens has been neglected and that with oxygens and methyl groups has been represented by the Lennard-Jones potential (Jorgensen, 1981).

Intramolecular potentials for water and methanol are based on the formulation proposed by Carney et al. (Carney et al, 1976). They are expressed as power series of the internal coordinates, ρ_i, 'stretch' and 'bend' and the three-body interactions are included:

$$V(\rho_i) = \sum L_{ij}\rho_i\rho_j + \sum L_{ijk}\rho_i\rho_j\rho_k + \sum L_{ijkl}\rho_i\rho_j\rho_k\rho_l \tag{2}$$

Usually in classical MD simulations the ion potentials are represented by the Coulomb and the Lennard-Jones terms. These potentials overestimate, however, the number of the solvent

molecules in the ion shells (Hawlicka & Swiatla-Wojcik, 2002) and underestimate a stability of the ion shells (Hawlicka & Swiatla-Wojcik, 2002, Bujnicka & Hawlicka, 2006). Moreover such potentials are inconsistent with flexible models of the solvent molecules. Therefore the ion-water and ion-methanol potentials were evaluated from *ab initio* calculations and fitted to the BJH and PHH models.

The potential energy for the complexes of the ion and the solvent molecule was computed for several hundred configurations of the complexes. Then the potential surfaces were fitted to the analytical form:

$$V_{i\alpha}(r) = \sum_{\alpha=1}^{3}\left[\frac{Q_{i\alpha}}{r} + \frac{A_{i\alpha}}{r^n} + B_{i\alpha}\cdot\exp(-C_{i\alpha}\cdot r)\right] \qquad (3)$$

where $Q_{i\alpha}$ represents the Coulombic interactions, which are defined by the ion charge and partial charges of the water or methanol molecules. The energies of the Coulombic interactions were subtracted from the potential surfaces. Parameters $A_{i\alpha}$, $B_{i\alpha}$ and $C_{i\alpha}$, were adjusted to the non-Coulomb part of the energy surface. They have no physical meaning. Parameters derived for ions, Na+(Marks et all, 1991; Hawlicka & Swiatla-Wojcik, 1995), Mg2+ (Dietz et al., 1982; Tamura et al., 1992), Ca2+(Probst et al., 185; Owczarek & Hawlicka, 2006), Cl- (Marks et all, 1991; Hawlicka & Swiatla-Wojcik, 1995) and the flexible molecules of BJH water and PHH methanol are summarized in Table 1.

The pair potentials for ions and solvent molecules are displayed in Figure 1 as a function of the ion-oxygen distance for the coplanar orientation shown in the insertion.
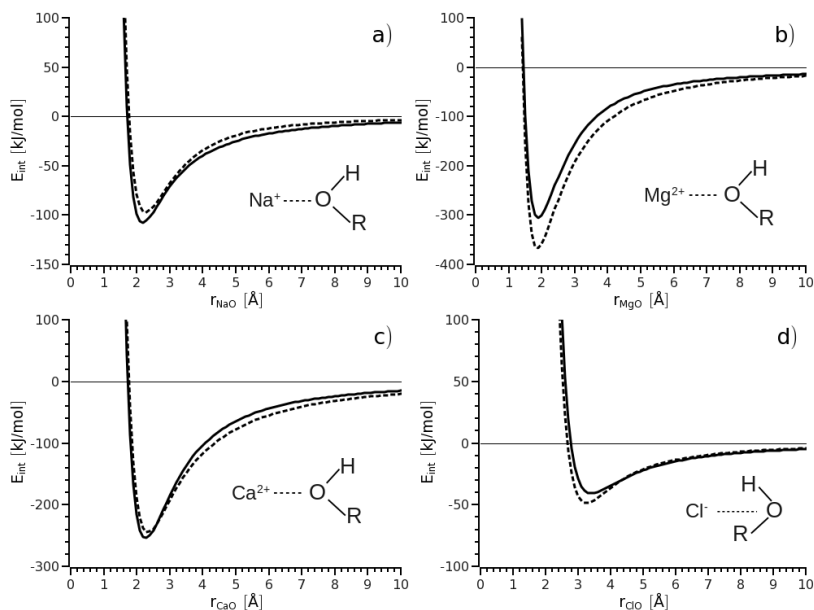

Fig. 1. Fitted pair potentials for the ion-water (solid) and ion-methanol (dashed) as function of the ion-oxygen distance for the orientation shown in the insertion.

i	α	$Q_{i\alpha}$ [kJ Å mol^{-1}]	$A_{i\alpha}$ [kJ Å^n mol^{-1}]	$B_{i\alpha}$ [kJ mol^{-1}]	$C_{i\alpha}$ [Å^{-1}]
Na	O_m	-833.61	-172.23	2.5328×10^5	4.1501
Na	H_m	486.27	593.40	-8.3289×10^2	0.9591
Na	Me	347.34	-274.90	5.1674×10^4	2.7930
Na	O_w	-916.28	-352.20	3.5555×10^5	4.2988
Na	H_w	458.14	151.60	5.1867×10^4	5.3919
Ca	O_m	-1667.30	-1372.63	2.5971×10^5	3.4900
Ca	H_m	972.58	933.29	8.3277×10^2	0.9600
Ca	Me	694.70	-474.95	5.1666×10^4	2.7930
Ca	O_w	-1832.56	-1572.66	2.5972×10^5	3.4900
Ca	H_w	916.28	626.41	1.2022×10^5	6.7900
Mg	O_m	-1667.30	-721.86	4.0778×10^5	4.3937
Mg	H_m	972.58	-7.21	4.2904×10^1	0.2749
Mg	Me	694.70	-232.28	1.8277×10^4	2.6485
Mg	O_w	-1832.56	-890.83	2.6954×10^5	4.0800
Mg	H_w	916.28	82.04	7.3844×10^1	0.3490
Cl	O_m	833.61	127.02	1.4532×10^5	3.1999
Cl	H_m	-486.27	-193.41	2.5091×10^4	3.3082
Cl	Me	-347.34	6.77	5.9262×10^5	3.2984
Cl	O_w	916.28	9.34	1.1750×10^5	2.6727
Cl	H_w	-458.14	-68.27	9.0210×10^4	4.5420

Table 1. Parameters $Q_{i\alpha}$, $A_{i\alpha}$, $B_{i\alpha}$ and $C_{i\alpha}$ in equation (3) for the interactions of ions with PHH methanol and BJH water.

As seen the interactions of the ion with molecules of the solvent components are similar. The lowest binding energies for ion-water and ion-methanol complexes are observed at the same distances. This position of the energy minimum is shifted to larger distance as the ionic radius increases (Marcus & Hefter, 2004) As might be expected the energy minimum becomes deeper when the charge density increases. The binding energy of Na$^+$ and Ca^{2+} ions with water is about 3% lower than that with methanol. An opposite features are found for of Mg^{2+} and Cl$^-$ ions, because their interactions with methanol are stronger than those with water. For Mg^{2+} ions the difference is about 10%, but for Cl$^-$ ions is less than 2%.

The pair potentials for interactions between ions were also derived from ab initio calculations. The potential energy surfaces were constructed from hundred configurations. Then they were fitted to the equation (3). Parameters were summarized in Table 2.

i	α	$Q_{i\alpha}$ [kJ Å mol^{-1}]	$A_{i\alpha}$ [kJ Å^n mol^{-1}]	$B_{i\alpha}$ [kJ mol^{-1}]	$C_{i\alpha}$ [Å^{-1}]	n
Na	Na	1389.4	-9.9154×10^2	1.0180×10^6	5.5909	6
Na	Cl	-1389.4	-7.9000×10^1	1.7172×10^5	3.1940	2
Ca	Ca	5557.6	-1.5198×10^4	2.6010×10^6	4.4870	6
Ca	Cl	-2778.8	-3.5301×10^2	3.6608×10^5	3.0100	2
Mg	Mg	5557.6	-1.4799×10^3	1.8226×10^6	6.3600	6
Mg	Cl	-2778.8	-2.0069×10^3	1.1854×10^5	2.6500	2
Cl	Cl	1389.4	-2.8672×10^4	9.1704×10^5	3.3863	6

Table 2. Parameters $Q_{i\alpha}$, $A_{i\alpha}$, $B_{i\alpha}$ and $C_{i\alpha}$ in equation (3) for the ion-ion interactions.

3. Radial distribution functions for the ions

Radial distribution function $g_{ion-\alpha}(r)$ represents the probability of finding the ion and α-site of the solvent molecule in a distance r, relative to the probability expected for a random distribution with the same density. These functions provide clear information about a structure of the ion surrounding. At room temperature the order is short-range thus the pair distribution function exhibits no more than two peaks. Positions of these peaks reflect average distances of neighbours in the first and second coordination shells.

Though the peak area is proportional to the number of the molecules in the shell, its height and width depend on a balance between the ion-solvent attraction and thermal motions of the solvent molecules. The first peak of the pair distribution functions increases with the increasing charge density, therefore it is generally higher and sharper for the cations than that for the anions and for the divalent ions than for the monovalent ions (Yu et al., 2010)

A surrounding of the ion in the methanol-water mixtures can be described by five radial distribution functions, two of them for the sites of water (O_w and H_w) and three for the sites of methanol (O_m, H_m and Me). The characteristic parameters of these functions are listed in Tables 3 and 4. There are positions of the first (R_{max1}) and second (R_{max2}) maxima, the positions of the first (r_{min1}) and second (r_{min2}) minima and the numbers of the particles in the first (n_1) and second (n_2) coordination shells.

The radial distribution functions of cation-oxygen in water, methanol and equimolar methanol-water mixture are shown in Figure 2. In aqueous solutions of MgCl$_2$ and CaCl$_2$ the cation-oxygen functions exhibit a sharp first peak, followed by broad second maximum. Positions of the first and second peaks coincide with the average distances of the first and second neighbours deduced from diffraction experiments (Ohtaki & Radnai, 1993). The $g_{NaOw}(r)$ function shows only one peak. As might be expected the position of the first peak is shifted to larger distances as the radius of the cation increases. The peak height depends on the charge density and the Mg^{2+}O$_w$ radial distribution function shows the highest peak.

Addition of methanol does not affect the position of the first maximum of the $g_{ionOw}(r)$ function. However the methanol addition increases the first peak, particularly that of the

x_M	ion	R_{max1}	$g(R_{max1})$	r_{min1}	n_1	R_{max2}	$g(R_{max2})$	r_{min2}	n_2
					oxygen				
0.0	Na	0.232	8.66	0.320	6.05	-	-	-	-
	Ca	0.237	15.65	0.340	10	0.430	2.82	0.552	27
	Mg	0.199	21.14	0.270	6.2	0.452	1.75	0.512	16
	Cl	0.335	2.98	0.398	8	-	-	-	-
0.1	Na	0.230	8.54	0.297	4.76	-	-	-	-
	Ca	0.240	18.67	0.300	9.70	0.440	2.80	0.564	23
	Mg	0.199	24.04	0.270	5.40	0.452	1.34	0.507	10
	Cl	0.337	2.23	0.410	5.80	-	-	-	-
0.5	Na	0.231	10.37	0.297	2.27	-	-	-	-
	Ca	0.237	35.88	0.305	6.80	0.450	2.38	0.558	7
	Mg	0.199	38.33	0.270	3	0.394	1.29	0.504	3
	Cl	0.344	1.10	0.386	1.04	-	-	-	-
0.9	Na	0.230	24.19	0.295	0.75	-	-	-	-
	Ca	0.232	105.93	0.310	2.30	-	-	-	-
	Mg	0.199	46.67	0.270	0.60	0.397	1.86	0.500	0.6
	Cl	-	-	-	-	-	-	-	-
					hydrogen				
0.0	Na	0.300	3.41	0.375	13.3	-	-	-	-
	Ca	0.307	5.93	0.380	20.0	0.500	1.41	0.620	59
	Mg	0.274	6.42	0.337	12.5	0.492	1.05	0.575	40
	Cl	0.242	2.50	0.310	7.38	-	-	-	-
0.1	Na	0.295	3.27	0.367	9.96	-	-	-	-
	Ca	0.312	7.57	0.382	19.4	0.512	2.28	0.620	51
	Mg	0.274	7.03	0.337	10.8	0.497	1.10	0.575	22
	Cl	0.242	1.86	0.310	4.96	-	-	-	-
0.5	Na	0.301	4.08	0.374	4.6	-	-	-	-
	Ca	0.312	30.69	0.382	13.6	0.518	3.50	0.623	15
	Mg	0.274	11.11	0.337	6.2	0.496	0.90	0.567	7
	Cl	0.251	0.87	0.306	1.06	-	-	-	-
0.9	Na	0.300	9.38	0.392	1.52	-	-	-	-
	Ca	0.310	42.35	0.370	4.5	-	-	-	-
	Mg	0.274	15.48	0.339	1.2	0.472	1.22	0.557	1
	Cl	-	-	-	-	-	-	-	-

Table 3. Characteristic parameters of the ion-water radial distribution functions: positions (in nm) of the first (R_{max1}) and second (R_{max2}) maxima, the first (r_{min1}) and second (r_{min2}) minima, heights of the first $g(R_{max1})$ and second $g(R_{max2})$ maxima and the first (n_1) and second (n_2) coordination numbers.

$Mg^{2+}O_w$ and $Ca^{2+}O_w$ functions. This may suggest that in mixed solvent the interactions of the cations with water molecules are favoured, despite similar binding energies of Ca^{2+} and Na^+ ions with methanol and water. This preference for water is observed also for Mg^{2+} ion, despite its stronger interactions with methanol than with water (see Figure 1 b). Moreover the first peak of the $g_{ionOw}(r)$ function increases, when the water content decreases. This is particularly remarkable for the Ca^{2+} ions and in the water deficit mixture, when the water

x_M	ion	R_{max1}	$g(R_{max1})$	r_{min1}	n_1	R_{max2}	$g(R_{max2})$	r_{min2}	n_2
					oxygen				
0.1	Na	0.237	15.46	0.317	1.25	-	-	-	-
	Ca	-	-	-	-	0.652	1.90	0.760	~5
	Mg	0.202	26.66	0.270	0.7	0.397	7.33	0.519	5
	Cl	0.325	14.09	0.410	2.25	-	-	-	-
0.5	Na	0.234	14.24	0.316	3.56	-	-	-	-
	Ca	0.252	5.75	0.332	1.7	0.478	3.05	0.555	8
	Mg	0.202	34.57	0.270	2.92	0.392	3.55	0.495	8
	Cl	0.324	9.84	0.414	6.10	-	-	-	-
0.9	Na	0.235	13.72	0.312	5.61	-	-	-	-
	Ca	0.250	15.60	0.347	5.7	0.480	3.47	0.565	~10
	Mg	0.202	46.67	0.270	5.4	0.399	3.17	0.472	7
	Cl	0.325	6.84	0.418	7.1	-	-	-	-
1.0	Na	0.238	15.90	0.340	5.8	-	-	-	-
	Ca	0.247	22.03	0.362	7.6	0.488	3.05	0.565	9
	Mg	0.202	50.22	0.270	6	0.397	3.35	0.472	7
	Cl	0.328	7.00	0.430	7.2	-	-	-	-
					hydroxyl hydrogen				
0.1	Na	0.282	7.29	0.380	1.25	-	-	-	-
	Ca	-	-	-	-	0.732	1.58	0.825	~5
	Mg	0.259	9.81	0.259	0.7	0.444	4.74	0.580	5
	Cl	0.227	27.12	0.312	2.20	-	-	-	-
0.5	Na	0.300	4.07	0.380	4.60	-	-	-	-
	Ca	0.337	2.96	0.419	1.7	0.545	2.38	0.623	~6.5
	Mg	0.262	11.91	0.262	2.92	0.492	2.28	0.574	9
	Cl	0.231	18.26	0.326	5.32	-	-	-	-
0.9	Na	0.290	5.86	0.385	5.59	-	-	-	-
	Ca	0.335	8.46	0.440	5.7	0.550	2.41	0.635	~12
	Mg	0.262	16.73	0.262	5.4	0.510	2.16	0.530	8
	Cl	0.235	13.56	0.335	6.70	-	-	-	-
1.0	Na	0.295	6.90	0.380	5.90	-	-	-	-
	Ca	0.332	11.90	0.400	7.6	0.562	2.19	0.635	~11
	Mg	0.262	17.98	0.262	6	0.505	2.19	0.522	8
	Cl	0.235	12.70	0.340	7.00	-	-	-	-

Table 4. Characteristic parameters of the ion-methanol radial distribution functions: positions (in nm) of the first (R_{max1}) and second (R_{max2}) maxima, the first (r_{min1}) and second (r_{min2}) minima, heights of the first $g(R_{max1})$ and second $g(R_{max2}$) maxima and the first (n_1) and second (n_2) coordination numbers.

content does not exceed 10 mol%, the first peaks of the $Ca^{2+}O_w$ function is about 7 times higher than that in aqueous solution (see Table 3). This suggests that in methanol rich solvents the Ca^{2+} shell contains several water molecules. The second maximum of the $g_{CaOw}(r)$ function shows also a distinct behaviour. In aqueous solution it is split into two peaks of similar heights, at 0.43 and 0.49 nm, respectively. When the methanol is added this splitting becomes less visible and vanishes in equimolar mixture.
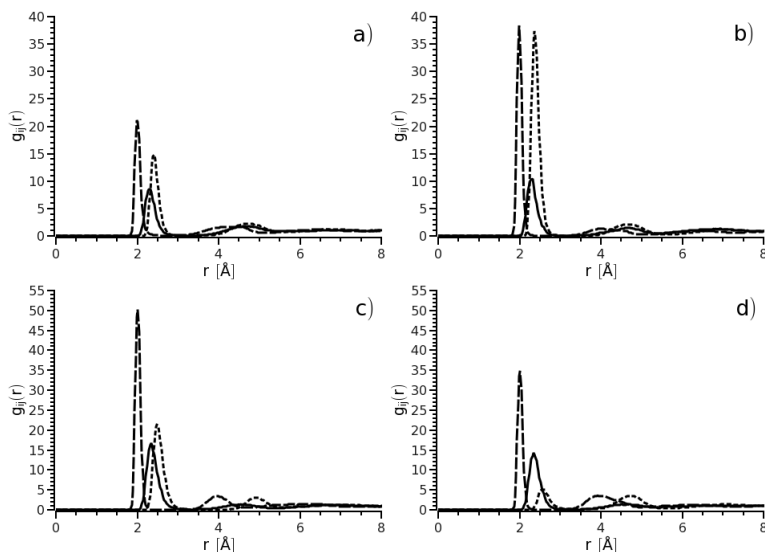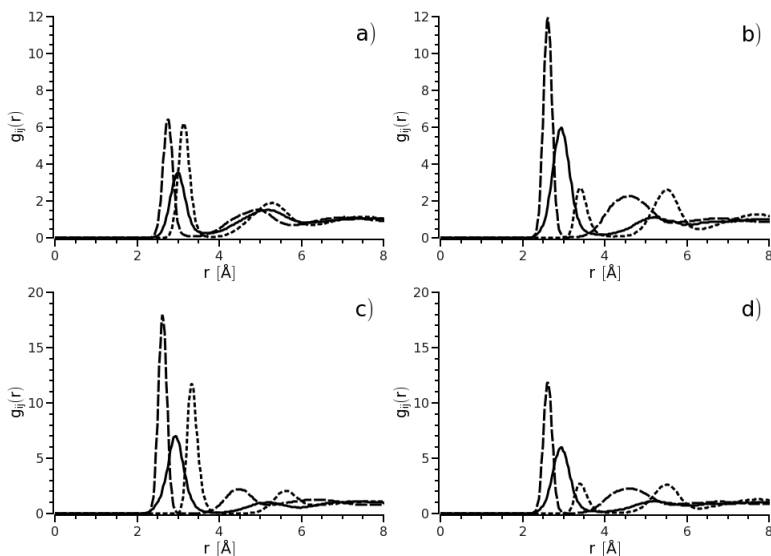
Fig. 2. Cation-oxygen radial distribution functions in solutions of NaCl (solid), MgCl$_2$ (dashed) and CaCl$_2$ (dotted) in water (a), methanol (c) and equimolar water-methanol mixture: oxygen of water (b) and methanol (d).

A comparison of the radial distribution functions for the cations in aqueous and methanolic solutions shows that the average distance to the methanol's oxygen is almost the same as to the water's oxygen. Such feature is in good agreement with the experimental results (Megyes et al., 2004; Neilsen & Enderby, 1979). The first peaks of all ion-oxygen functions in methanolic solutions are higher that those in aqueous solutions. This suggests that positions of the methanol molecules in the cation shells are more restricted than those of water molecules. As seen from Table 4 the height of the $g_{ionOm}(r)$ peak decreases when the methanol content decreases. A striking behaviour has been notice for calcium ions. In water rich mixture, for the methanol content 10 mol%, the first and second maxima of the $g_{CaOm}(r)$ function, expected at 0.25 and 0.49 nm, are absent. This suggests that the methanol molecules do not enter the first and even the second coordination shell of Ca^{2+} ions, despite very similar energy of interactions (see Figure 1c).

Radial distribution functions of the cations and the hydroxyl hydrogens of water and methanol are shown in Figure 3.

The cation-hydroxyl hydrogen functions coincide with the cation-oxygen pair distribution functions. Therefore is not surprising that the positions of the sharp first peak of $g_{ionH}(r)$ do not depend on the methanol content. As seen from Tables 3 and 4 the cation-hydroxyl hydrogen distance is longer, by about 0.07 nm, than that of the water's and methanol's oxygen. This suggests an antidipole orientation of the solvent molecules in the first coordination shells of the cations. The radial distribution functions for the cations and the methyl group are not shown, because a direct correlation between these sites is lacking.

Radial distribution functions computed for chloride ions in the solutions of NaCl, MgCl$_2$ and CaCl$_2$ are very similar, therefore the pair distribution functions, computed for CaCl$_2$

solutions are displayed in Figure 4 as the example of the Cl^--oxygen and Cl^--hydroxyl hydrogen pair distribution functions.

Fig. 3. Cation-hydroxyl hydrogen radial distribution functions in solutions of NaCl (solid), $MgCl_2$ (dashed) and $CaCl_2$ (dotted) in water (a), methanol (c) and equimolar water-methanol mixture: oxygen of water (b) and methanol (d).

In aqueous and methanolic solutions of NaCl, $MgCl_2$ and $CaCl_2$ the first peak of the Cl^- O_w and Cl^- O_m functions is centred at 0.33 nm. This agrees with the average distance, deduced from X-ray diffraction, from the Cl^- ion to oxygens in aqueous (Yu et al., 2010) and methanolic (Megyes et al., 2004; Neilsen & Enderby, 1979) solutions. Position of the $g_{ClHw}(r)$ and $g_{ClHm}(r)$ functions, at 0.242 nm, coincides with the anion-oxygen distance. This shorter, by about 0.09 nm, distance suggests almost linear hydrogen bond between the anion and the solvent molecules. In aqueous solutions the first peaks of the $g_{ClOw}(r)$ and $g_{ClHw}(r)$ functions are not distinctly separated from the bulk. This evidences a high flexibility of the hydrated anion and suggests an easy exchange of the water molecules between the coordination shell and the bulk solvent. In methanolic solutions the peaks of the $g_{ClOm}(r)$ and $g_{ClHm}(r)$ functions are higher and better pronounced. This may indicate that the coordination shell of the anion in methanolic solutions is more stable.

The composition of the mixed solvent does not affect the peak positions, but it influences remarkably the peak height. The changes of the peak height follows the changes of the solvent components, therefore the $g_{ClOm}(r)$ and $g_{ClHm}(r)$ peaks increase and the $g_{ClOw}(r)$ and $g_{ClHw}(r)$ peaks should decrease with the increasing methanol content. However the influence of the solvent composition on the Cl^--water radial distribution function is more dramatic. In equimolar mixture the first peaks of the $g_{ClOw}(r)$ $g_{ClHw}(r)$ functions, expected at 0.33 and 0.242 nm, respectively, are absent. This means that the coordination shells of the anions do not contain the water molecules. This is observed despite the very similar energy interactions of the Cl^- ion with water and methanol molecules (see Figure 1d).
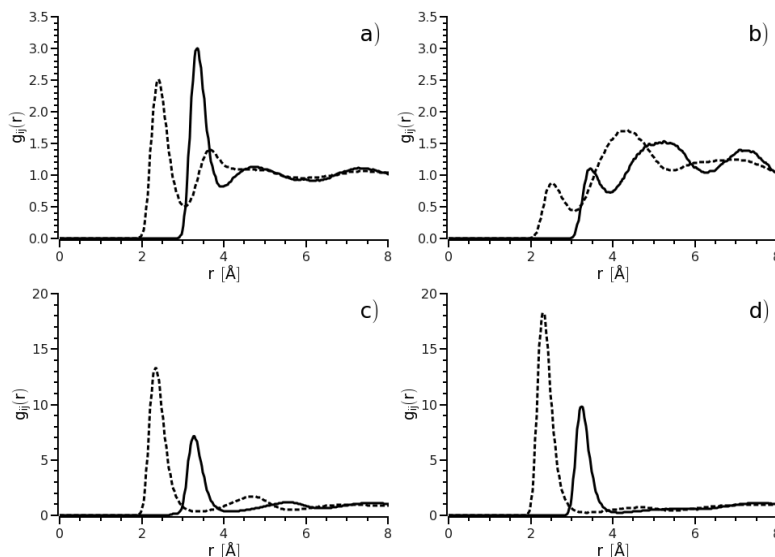
Fig. 4. Radial distribution functions for Cl⁻ and water and methanol sites: oxygen (solid) and hydroxyl hydrogen (dotted). Solutions of CaCl₂ in water (a), methanol (c) and equimolar water-methanol mixture: water's (b) and methanol's (d) sites.

4. Coordination numbers of the ions

The numbers of the α-sites in the coordination shells are equal to the running integration numbers, which have been computed by the integration of the $g_{ion\alpha}(r)$ function within the boundaries of the shell, r_1 and r_2, respectively.

$$n_\alpha = 4\pi\rho_\alpha \int_{r_1}^{r_2} g_{ion\alpha}(r) r^2 dr \qquad (4)$$

where ρ_α denotes the number density of the α-sites. The boundaries of the shells correspond to the minima of the g(r) functions. Well-separated peaks of the radial distribution functions for the cations permit to compute unambiguously the number of the molecules in the first and even in the second shell. The number of the solvent molecules in the Cl⁻ shell is not certain, because the peaks are badly pronounced.

Diffraction experiments have shown that sodium and magnesium ions are six-coordinated both in aqueous (Ohtaki&Radnai,1993) and methanolic (Megyes et al., 2004) solutions. The hydration number of Ca²⁺ is greater, it strongly depends on the salt concentration and covers a wide interval, from 10.7 to 5.5 (Yamagouchi et al., 1989). The salt concentration influences also the number of the methanol molecules coordinated by Ca²⁺, but this dependence is weaker (Megyes et al., 2004).

Coordination numbers of Na⁺ and Mg²⁺, obtained from MD simulations, agree with the experimental results. Despite higher charge density of Mg²⁺ both cations, Na⁺ and Mg²⁺, are

six-coordinated in aqueous and methanolic solutions. Thus the coordination number should be independent of the solvent composition. Though the charge density of Ca^{2+} is smaller than that of Mg^{2+}, the first shell of Ca^{2+} is larger. In aqueous solution the Ca^{2+} shell consists of 10 water molecules. In methanolic solution the Ca^{2+} shell contains less molecules. The coordination number is 7.6. This means that the Ca^{2+} shells contain either seven or eight methanol molecules. Thus one may expect that the methanol addition will slightly reduce the coordination number of Ca^{2+}.

In aqueous solutions of NaCl, $MgCl_2$ and $CaCl_2$ the chloride ion coordinates about eight water molecules. Smaller hydration number, about 6, was deduced from the X-ray experiments (Yu et al., 2010) Such discrepancy can be understood, because the hydration shell of the anion is badly pronounced. In methanolic solution the Cl^- ion coordinates less molecules, about 7. Different coordination numbers of Cl^-, six (Megyes et al., 2004) and more than seven (Yamagouchi et al., 1989) have been deduced from X-ray scattering in methanol solutions of $CaCl_2$ and $MgCl_2$. The discrepancy might be due to the higher concentration of the experimentally examined solution.

Interactions of the ions with water and methanol are very similar (see Figure 1) therefore a selective solvation of the ions has been not expected. The inspection of the results listed in Tables 3 and 4 shows, however, that the influence of the methanol addition on the composition of the ion shells can be dramatic. To describe this effect the real composition of the ion shells has been compared with the expected composition.

The 'real' methanol mole fraction in the first and second coordination shells of the ions has been computed as follows:

$$(x_m)_{obs} = \frac{(n_m)_k}{(n_m)_k + (n_w)_k} \tag{5}$$

where $(n_w)_k$ and $(n_m)_k$ are the running integration numbers of the methanol and water molecules, respectively, computed for the first or second coordination shells.

The number density of the methanol and water molecules in the mixture depends nonlinearly on the methanol mole fraction. Therefore even when the preferential solvation of ions does not occur, the methanol concentrations in the coordination shell and the bulk solvent are not the same. Assuming a lack of the selective solvation, the expected mole fraction of methanol in the ion shell can be calculated as follows (Hawlicka & Switla-Wojcik, 2000):

$$(x_m)_{exp} = \frac{(n_m)_o \dfrac{\rho_m(x_m)}{(\rho_m)_o}}{(n_m)_o \dfrac{\rho_m(x_m)}{(\rho_m)_o} + (n_w)_o \dfrac{\rho_w(x_m)}{(\rho_w)_o}} \tag{6}$$

$(n_w)_o$ and $(n_m)_o$ are the numbers of the coordinated solvent molecules in pure water and methanol, $(\rho_w)_o$ and $(\rho_m)_o$ denote the number densities of the solvent components in the aqueous and methanolic solutions of the salts, while $\rho_w(x_m)$ and $\rho_m(x_m)$ are the number densities of water and methanol, respectively, in ternary systems: salt-methanol-water.

The non-linear changes of the mixed solvent density should give a slight excess of methanol in the primary coordination shells of the ions. The results of MD simulation show, however, significant deviations of the real composition of the ion shells. This suggests a selective solvation of the ions. To demonstrate the preferences of the ions the observed methanol mole fraction, $(x_m)_{obs}$, is shown as the function of the expected methanol mole fraction $(x_m)_{exp}$ in Figure 5.

The content of methanol in the first coordination shells of Ca^{2+} and Mg^{2+} ions is remarkably smaller than expected. Thus the Ca^{2+} and Mg^{2+} ions favour water molecules in their shells. As seen from Figure 5 the preferential hydration of these cations is observed over whole range of the mixture composition. The Na^+ ion also favours the water molecules in its primary shell, but this inclination is weaker, therefore the preferential hydration occurs only in the water deficit mixtures. This agrees with experiments, which have shown the equality of the self-diffusion coefficients of water and Na^+ ions in water deficit mixtures (Hawlicka, 1986). The self-diffusion experiments have also shown that the addition of $CaCl_2$ to the methanol water-mixture does not influence the methanol self-diffusion coefficient, but it reduces strongly the water self-diffusion coefficient (Palka & Hawlicka, 2004) . This means that translations of the cation and water molecules are correlated, because these species form an aggregate.
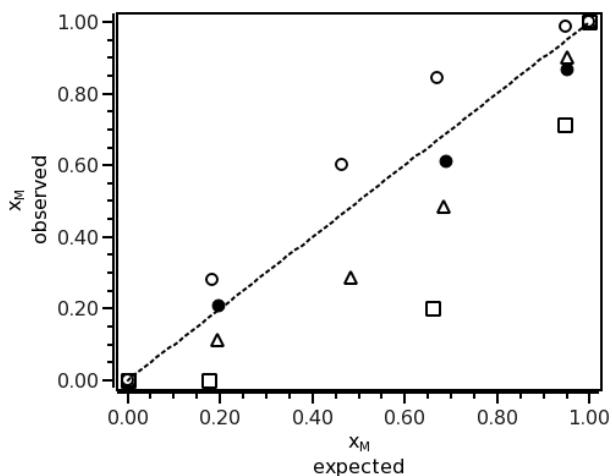
Fig. 5. The dependence of the observed methanol mole fraction in the primary shell of Na^+ (●), Mg^{2+} (Δ), Ca^{2+} (□) and Cl^- (○) ions on the expected methanol mole fraction.

Though all cations favour water molecules in the nearest surrounding, some difference should be noticed. The Mg^{2+} shells contain about 10% more water than expected, the significant excess is observed only in equimolar mixture. The Ca^{2+} ions exhibit the stronger preference for water, because in the water deficit region the calcium ion coordinates most of the water molecules. Moreover the Ca^{2+} ion favours the water molecules also in its second shell. In water rich mixture both shell of the Ca^{2+} ions consist only of the water molecules. Preferences of the Mg^{2+} and Na^+ ions in their second shells are opposite and an excess of the methanol content is observed.

Interactions of the chloride ions with methanol and water are weaker than those of cations. The coordination shell of Cl- is flexible, but its composition differs significantly from that of the bulk solvent. The chloride ions favour methanol molecules in their coordination shells. This preference is observed in solutions of NaCl, CaCl$_2$ and MgCl$_2$, over the whole range of the composition of the mixed solvent. The preferential solvation of Cl- by methanol has been postulated from self-diffusion coefficients. The diffusion experiments have shown that in methanol rich solvents translations of the chloride ions and methanol molecules are strongly correlated (Hawlicka, 1986). The Cl- ion favours the methanol molecules in its primary shell despite very similar binding energies of the anion with the solvent components.

5. Orientation of the solvent molecules in the first coordination shell

Orientation of the molecules around the ion can be characterised by an angle θ between the vector connecting the ion with the oxygen and the dipole moment of the solvent molecule. The angular distribution functions are shown in Figure 6.
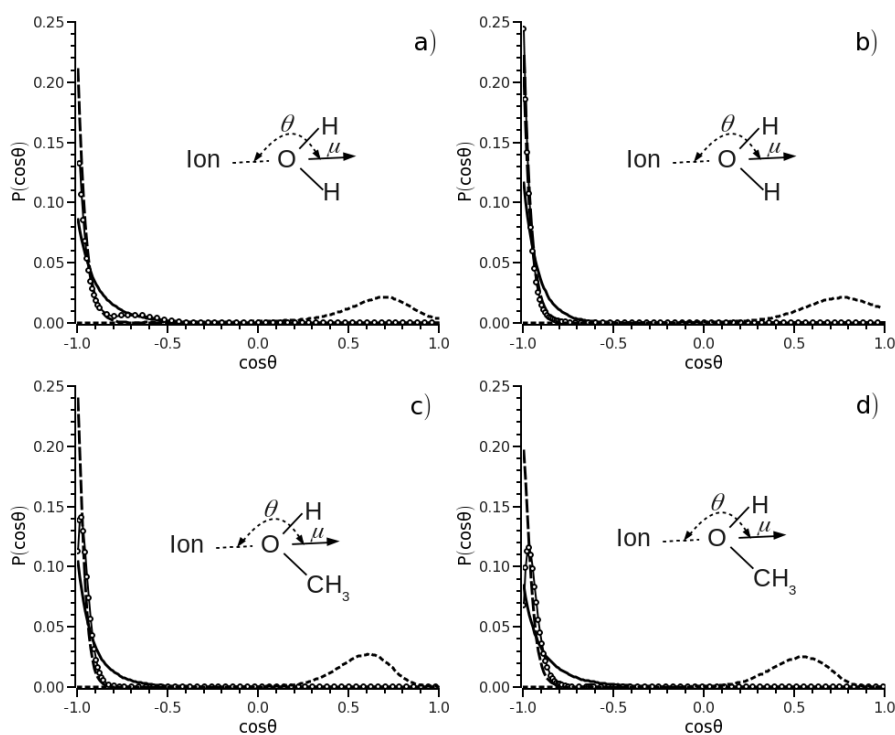
Fig. 6. Distribution functions of angular orientation of the nearest neighbours of Na+ (solid), Mg^{2+}(dashed), Ca^{2+} (○) and Cl- (dotted) in water (a), methanol (c) and equimolar mixture (b, d). The angle θ defined in the inset.

Distribution functions of the angular orientation of the water molecules in the primary shells of Na+, Mg^{2+} and Ca^{2+} ions show the peak centred at cosθ = -1. This indicates that the

antidipole orientation of the water molecules in the cation shells dominates. The distribution of the θ angle for Mg^{2+} is narrower than those for Na^+ and Ca^{2+}. This is not surprising that the water molecules are better oriented in the field of Mg^{2+}, which is stronger than the fields of Na^+ and Ca^{2+}. The primary shell of Ca^{2+} contains more water molecules than the shells of the six-coordinated Na^+ and Mg^{2+} ions, therefore the angular distribution for Ca^{2+} shows a shoulder for $\cos\theta \cong -0.7$. This means that the dipole moments of a few water molecules in the Ca^{2+} shell are tilted, by about 45°, from the antidipole orientation. This 'improper' orientation vanishes in equimolar mixture when the coordination number decreases from 10 to 7. This suggests that the coordination shell of Ca^{2+} is compact.

The antidipole orientation of the methanol molecules is also observed in the Na^+ and Mg^{2+} shells. A different orientation has been noticed for the methanol molecules in the Ca^{2+} shell. The distribution of the O-Ca^{2+}O angles, shows the dominant peak at $\cos\theta$ =-0.9. Thus the dipole moments of the methanol molecules in the Ca^{2+} vicinity are tilted by about 25°.

As might be expected the orientation of the solvent molecules in the vicinity of chloride ions is different. The distance from the anion to oxygen is longer than that to hydrogen. This suggests a hydrogen bond between the anion and the nearest solvent molecules. In aqueous and methanolic solutions the dominant peaks of the angular distributions are centred at $\cos\theta$=0.68. This confirms that H-bond between the anion and solvent molecules is almost linear. As might be expected the orientation of the solvent molecules in the anion shell for all studied solutions is independent of the solvent composition.

To describe a geometrical arrangement of the solvent molecules in the solvation shells two angles can be defined. The φ angle is the angle between two vectors pointing from the ion to the nearest oxygens. The ψ angle, which is the angle between the three oxygens, permits to deduce a difference between the order of the water molecules in the coordination shells and the tetrahedral structure of water. The distributions of the φ angles have been computed without any distinction between oxygens belonging to water and methanol molecules. The results are displayed in Figure 7.
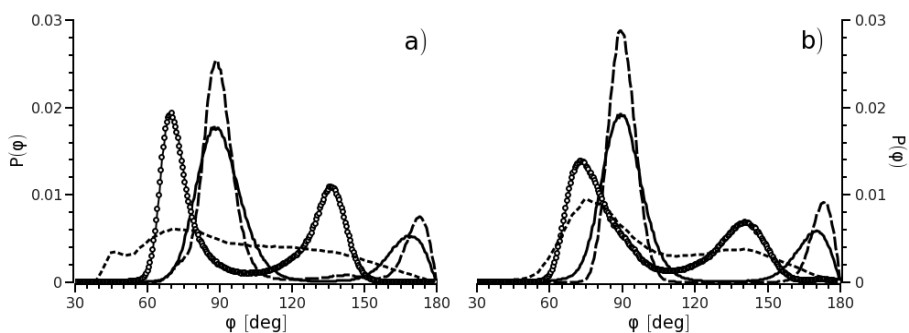

Fig. 7. Distribution of φ angles, for the water (a) and methanol (b) molecules in the primary shells of Na^+ (solid), Mg^{2+}(dashed), Ca^{2+}(○) and Cl^- (dotted).

The distribution of φ angles computed for the coordination shells of the Na^+ and Mg^{2+} ions is independent of the solvent composition. Two peaks, centred at 90° and 180°, indicate that the water and methanol molecules form an octahedron around the cation. The distribution

of the angles between three oxygens of the solvent molecules in the Na^+ and Mg^{2+} shells shows two peaks at 60 and 90°, respectively. This confirms the octahedral arrangement of the coordination shells.

The Ca^{2+} shell, which contains more molecules, does not show any symmetry. As seen from Figure 7 in aqueous solution the distribution of $O-Ca^{2+}-O$ angles exhibits two peaks, around 67° and 135°, respectively. The former angle is close to the value, which can be expected for tetrahedral or hexahedral symmetry, but the latter angle cannot be correlated with any of the polyhedra. This means that the Ca^{2+} shell is irregular. When the coordination number of Ca^{2+} decreases with the increasing methanol content, the most probable $O-Ca^{2+}-O$ angle increases. In methanolic solution the distribution of φ angles shows two peaks around 75° or 145°, respectively. This means that the cation shell remains irregular. The distribution of the O-O-O angles confirms a lack of symmetry of the Ca^{2+} shell, because in all studied solutions these angles are either 55° or 107°.

The $O-Cl^-$-O angles, computed for the solutions of NaCl, $MgCl_2$ and $CaCl_2$, are very similar. As seen from Figure 7 the distribution of the $O-Cl^-$-O angle is almost uniform. This means that the coordination shell does not show any symmetrical arrangement. A lack of the symmetry of the Cl^- shell causes that in aqueous solution the distribution of the O-O-O angles is almost uniform, except a small peak at about 54°. It is worthy to notice that such peak is believed to be a distinctive feature of the tetrahedral arrangement of pure water (Gallanger & Sharp, 2003). This means that in the coordination shell of Cl^- the water structure partially remains.

6. Residence time of the solvent molecules in the coordination shells

An important feature of ions in solutions is a persistence of the coordination shell, because a dynamics of an exchange process may determine a reaction rate. A residence time of the solvent molecules in the coordination shells of the ions has been calculated from a time correlation function R(t), proposed previously (Impeay et al., 1983). The time correlation function is defined as follows:

$$R(t) = \frac{\sum_{i=1}^{N\alpha}\sum_{j=1}^{N_\beta}\kappa_{ij}(t)\cdot\kappa_{ij}(t+\Delta t)}{N_\alpha \cdot N_\beta} \tag{7}$$

where N_α and N_β denote the number of ions and the solvent molecules in the sphere of the radius defined by the first minimum of the $g_{ionO}(r)$ function, respectively. $\kappa_{ij}(t)$ is the step function; $\kappa_{ij}(t)=1$, if the solvent molecule j is in the ion shell and $\kappa_{ij}(t)=0$ otherwise. The calculations of the R(t) functions were performed for at least 500 randomly chosen initial configurations. The calculations were done for several time intervals Δt within the range 0.01-0.5 ps.

The solvent molecules could leave the ion shell for a period, which was shorter than Δt, otherwise they were neglected in further calculations. Variations of Δt and the solvent composition do not influence the character of R(t) functions. For all simulated systems the time correlation functions for Mg^{2+} and Ca^{2+} ions decrease rapidly in the period shorter than

1 ps, afterward, independently of the time interval, they reach a constant value close to 0.95. This means that about 95% of the solvent molecules do not leave the coordination shells of the cations during the whole simulation time. The coordination shells of the divalent cations are very stable, with the lifetime remarkably exceeding 150 ps, and being independent of the solvent composition. The long lifetime of the primary hydration shells has been reported previously for Ca^{2+}, about 700 ps, and Mg^{2+}, about 422 ps (Konesham et al., 1998). The long residence time of the solvent molecules has been expected, because the hydrodynamic radii of both cations noticeably exceed the ion radii in crystal (Hawlicka, 1995). This means that the cations move with their coordination shells together, because the ion filed controls the translations of all nearest neighbours.

The R(t) functions for the Na^+ and Cl^- ions decrease monotonously and they can be fitted to a second-order exponential decay:

$$R(t) = A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2}) \tag{8}$$

The first term describes an escape of the solvent molecules located close to the border of the coordination shell, whereas the second term concerns the persistence of the shell. Parameters A_1 and A_2 reflect fractions of the solvent molecules involved in both processes. The first process is rather fast and its characteristic time τ_1 is shorter than 1 ps. The residence time τ_2 of the solvent molecules in the Cl^- shell and the methanol molecules in the Na^+ shell increase with the time interval Δt. Such dependence it is shown in Figure 8.
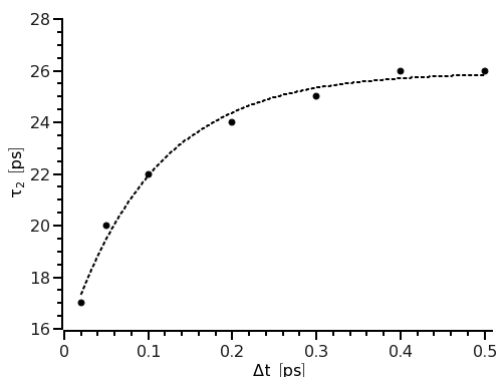

Fig. 8. Influence of the time interval Δt. on the residence time τ_2 of the methanol molecules in the Cl^- shell.

As seen the residence time reaches the constant value when Δt is not shorter than 0.2ps. Thus the τ_2 values discussed below were computed for Δt=0.2 ps. This means that the solvent molecules leaving the ion shell for the time longer than 0.2 ps were neglected in further calculations.

In aqueous solution the lifetime of the coordination shell of Na^+ is long, more than 170 ps, but in methanolic solution this time is much shorter, about 45 ps. Therefore is not surprising that the lifetime of the Na^+ shell decreases when the methanol content increases.

The exchange of the water molecules between the Cl⁻ shell and the bulk is fast. Though the size and composition of the anion shell in solutions of $CaCl_2$, $MgCl_2$ and NaCl are the same, the persistence of the shells is different. In solutions of $CaCl_2$ and $MgCl_2$ the anion shells are more flexible than those in NaCl solutions. In solutions of the alkali earth chlorides about 85% of the water molecules stay in the primary shell of the anion less than 5 ps. This means that the water residence time is shorter than the characteristic time of the water translations, about 6 ps (Hawlicka & Switla-Wojcik, 2000). This explains why the hydrodynamic radius of Cl⁻ in aqueous solution is like its radius in crystal (Hawlicka, 1986). In NaCl solution the lifetime of the anion shell is longer. About 75% of the water molecules stay in the shell about 19 ps.

The residence time of the methanol molecules in the Cl⁻ shell is longer than that of the water molecules. In methanolic solutions of $CaCl_2$ and $MgCl_2$ the lifetime of the Cl⁻ shell exceeds 50 ps. Shorter lifetime, about 25 ps, has been found for the methanolic solution of NaCl. However even this shortest residence time, 25 ps, exceeds significantly the characteristic time of methanol translations, about 9 ps (Hawlicka & Switla-Wojcik, 2000). This explains why the hydrodynamic radius of Cl⁻ in net methanol is greater than the radius in crystal (Hawlicka, 1986).

7. H-bonds of the solvent molecules in the first coordination shell

Comparison of the number of the solvent molecules in the first and second coordination shells suggests that in aqueous solutions and water rich mixtures, almost any water molecule in the primary shell of Mg^{2+} has at least two neighbours in the second shell. Such result seems to be consistent with the antidipole orientation of these molecules. The orientation of the water molecules in the first shell of Ca^{2+} is less restricted therefore it is not surprising that they have three neighbours in the second shell. Number of the second neighbours of Na^+ is difficult to determine, because the second shell is not stable and the second peak of the Na^+O radial distribution function is lacking.

With increasing methanol content the number of the neighbours in the second shells of Mg^{2+} and Ca^{2+} decreases rapidly and in equimolar mixture the water or methanol molecule in the first shell has only one neighbour in the second shell. A question is whether the molecules in the primary shell are hydrogen bonded with those in the second shell or in the bulk.

In MD simulation all pair interactions change continuously as a function of the separation and orientation of the molecules therefore there is no unambiguous definition of the hydrogen bond. Usually two definitions, either energetic or geometric, of the H-bond are considered. The energetic criterion of H-bond, based on the pair interaction energy, treats two molecules as H-bonded, if their interaction energy is less than –8 kJ·mol⁻¹. This criterion coincides with the geometric definition, which considers two molecules as H-bonded, if the distances between two oxygens and between the hydrogen and oxygen of the H-bond acceptor do not exceed 0.350 and 0.250 nm, respectively, and if the angle between the OH intramolecular bond of the H-donor and the line connecting the oxygens is less than 30° (Hawlicka & Swiatla-Wojcik, 1998).

The average numbers of the H-bonds were computed in 0.001 ps intervals over the whole simulation runs. The average number of H-bonds per water molecule in pure water is $<n_{HB}>_w$=3.5. Addition of electrolytes, NaCl, $MgCl_2$ and $CaCl_2$, reduces slightly this number.

In all studied solutions the H-bond numbers are the same, $<n_{HB}>_w$=3.1. Thus this influence is slight and only in $CaCl_2$ solutions it extends beyond the first coordination shells of the ions (Owczarek et al., 2007).

Differences between the electrolyte solutions appear when the H-bonds of the molecules in first coordination shell of the cations are compared. The Mg^{2+} and Na^{2+} ions are six-coordinated and the angular distributions show, that all water molecules are properly oriented to form two H-bonds as H-donors. Though the average number of H-bonds per the water molecule in the Na^+ shell is two, $[<n_{HB}>_w]_{Na^+}$=2, a detailed analysis shows that about 65% of the water molecules in the Na^+ shell form 2 H-bonds, whereas the reminder of them has either one, about 15%, or three, about 20%, H-bonded neighbours. Most of the water molecules in the Mg^{2+} shell, about 70%, have two H-bonded neighbours, but 30% of the molecules form only one H-bond. Though both cations coordinate six water molecules the radius of Mg^{2+} shell is smaller, about 0.27 nm, than that of the Na^+ shell, about 0.32 nm. Thus the Mg^{2+} shell must be more compact and there is probably not enough space for H-bonded neighbours of all water molecules. The water molecules in the Ca^{2+} shell have also less H-bonded neighbours. Most of them, about 80%, has only one H-bonded neighbour and only 20% of the molecules form two H-bonds with their neighbours in the second shell. The radii of Ca^{2+} and Na^+ ions in crystal, 0.096 and 0.102 nm (Marcus & Hefter, 2004) and their shells, 0.34 and 0.32 nm respectively (see Table 3), are similar. The first shell of Ca^{2+} consists however of 10 water molecules. Though most of them are oriented properly to have the H-bonded neighbours the shell is compact and only 20% of the molecules have enough space for two H-bonded neighbours in the second shell.

In mixed solvent the number of H-bonds per water molecule in the shells of Na^+ and Mg^{2+} ions remains unchanged. Such behaviour might be expected, because neither the coordination number nor the orientation of the molecules depends on the solvent composition. In methanol-water mixtures the water molecules from the first shells of Na^+ and Mg^{2+} prefer the methanol molecules as H-bonded neighbours in the next sphere. Such preference can be understood, because the H-bond between the H-donor water molecule and the H-acceptor methanol molecule is energetically favourable (Palinkas et al. 1991).

As seen from Tables 3 and 4 the number of the molecules in the first and second shells of Ca^{2+} decrease with the increasing methanol content. The radii of both shells are, however, independent of the mixture composition. Thus the first shell becomes less compact. This improves the orientation of the water molecules as H-donors. In consequence all water molecules have two H-bonded neighbours. However they have water molecules as the H-bonded neighbours despite the unfavourable energy of H-bond between two water molecules. The methanol molecules appear in the first shells of Ca^{2+} in methanol rich solvents, when there is a lack of water to form the coordination shell. Their antidipole orientation causes that they have only one H-bonded neighbour.

The chloride ion is H-bond acceptor and in aqueous solution the water molecules form almost linear H-bond with Cl^- shell. About 80% of the water molecules coordinated by the anion form three H-bonds with the neighbours in the bulk solvent. In mixed solvent the methanol molecules replace the water molecules in the anion shell. The molecules form the linear H-bond with Cl^- therefore they are H-acceptors and have only one H-bonded neighbour in the bulk solvent.

An interesting question is how does the ionic field influence a strength and persistency of the H-bonds. To describe this effect the average H-bond energy of the molecules in the ion shells was calculated and it was compared with the average H-bond energy computed for the mixed solvent. The average energy of two H-bonded molecules in liquid BJH water, $<E_{HB}>_w$= -17.3 kJ·mol^{-1}, is of about 10% higher than the energy of two H-bonded molecules in liquid PHH methanol, $<E_{HB}>_w$= -19.2 kJ·mol^{-1}. Such feature agrees with the difference of the binding energies of water and methanol dimers (Palinkas et al. 1991). In gas phase the binding energies for the dimer of unlike molecules depends on the configuration of the water and methanol molecules. The H-bond between the H-acceptor methanol molecule and H-donor water molecule is energetically favourable (Palinkas et al., 1991). Therefore the average energy of the H-bond in the methanol-water mixtures decreases with the increasing methanol content (Owczarek et al., 2009). In liquid mixtures the energies of two different configurations are slightly different and the energy of the H-acceptor methanol and H-donor water is lower by about 7%.

The influence of the anionic field on the strength of H-bonds is negligible and the H-bond energy of the water and methanol molecules, coordinated by the Cl$^-$ ions, does not differ from the H-bond energy in the bulk solvent. A lack of the influence can be understood, because the charge density of the chloride ion is small, therefore the anion field does not polarise the solvent molecules.

The charge densities of the cations are higher, particularly of Mg^{2+}, and their field polarises the solvent molecules. In such case a strengthening of the H-bonds might be expected. Indeed the energies of the H-bonds of the water molecules coordinated by the cations are lower than the energy of the H-bonds in the bulk solvent. As might be expected the influence of the Mg^{2+} field is the strongest one and the H-bond energy is lower by about 20%, than that in the bulk. The H-bond energy of the water molecules coordinated by Na$^+$ and Ca^{2+} ions is lower, by about 10%, as compared with that in the bulk solvent. The influence of the Ca^{2+} and Na$^+$ fields seems to be very similar, despite different charge densities, but it is worthy to stress that the second neighbours of these cations are different. The Ca^{2+} ion favours the water molecules in both shells and such H-bonds are weaker as compared with those between the water molecules in the Na$^+$ shell and its second neighbours, the methanol molecules.

To describe an influence of the ionic field on a persistence of the H-bonds a lifetime of H-bonds of the molecules in the first shells was computed and compared with that in binary solvent. From among various concepts of the H-bond lifetime an approach proposed previously (Rappaport, 1983) was adopted. The concept of so-called 'continuous lifetime' takes into account only the unbroken H-bonds. This means that the H-bond once broken and then renewed is neglected. The lifetime of H-bonds was computed from the time correlation function R(t), defined above by the equation (7). In these calculations N_α and N_β denote the number of ions and the H-bonds, respectively, and $\kappa_{ij}(t)$ is the step function. If the solvent molecule j was H-bonded than $\kappa_{ij}(t)$=1 and otherwise $\kappa_{ij}(t)$=0. The calculations of the R(t) functions were performed for at least 500 randomly chosen initial configurations. The H-bonds were monitored in 0.001 time intervals. This short time interval is consistent with hindered rotations of the solvent molecules (Roberts et al., 2009), which may destroy the H-bond. The R(t) functions can be fitted to the first-order exponential decay.

At room temperature the continuous lifetime of H-bonds in pure water is about 0.3 ps, it increases linearly with the increasing methanol content and reaches about 1.5 ps in pure

methanol. The influence of the ionic field on the H-bond lifetime is minor. The cationic field slightly stabilizes the persistence of the H-bonds. The lifetime of the H-bonds of the water and methanol molecules in the cation shells is by about 20% longer. The influence of the anion filed is opposite and the lifetime of the H-bonds is slightly shorter than in the bulk solvent.

8. Influence of the ions on intramolecular vibrations

Total spectral densities S(ω) of water and methanol have been calculated as the sum of partial densities $S^\alpha(\omega)$ of sites α (α= O, H, H for water and O, H, Me for methanol):

$$S(\omega) = \sum_{\alpha=1}^{3} S^\alpha(\omega) \qquad (9)$$

where ω denotes the frequency of vibrations given in wave number (cm^{-1}). The partial densities $S^\alpha(\omega)$ have been obtained via Fourier transform of the normalized velocity autocorrelation function:

$$S(\omega) = \frac{2m_\alpha c}{kT} \int_0^\infty C_{vv}^\alpha(t) \cos(2\pi c\omega t) dt \qquad (10)$$

where m_α is mass of the α site, c and k denote the light velocity and Bolzmann's constant, respectively. The normalized velocity autocorrelation function is defined as follows:

$$C_{vv}^\alpha(t) = \frac{1}{N_t N_\alpha C_{vv}^\alpha(0)} \sum_{i=1}^{N_t} \sum_{j=1}^{N_\alpha} \vec{v}_j^\alpha(t_i) \cdot \vec{v}_j^\alpha(t_i + \Delta t) \qquad (11)$$

where N_t and N_α denote the numbers of the time averages and sites, respectively, $v_j^\alpha(t_i)$ is the velocity of the site j of the kind α at the time t_i and $C_{vv}^\alpha(0)$ represents the normalization factor.

Basic frequencies obtained from MD simulation for the liquid BJH water are 1716 cm^{-1} and 3533 cm^{-1} for the HOH bending and OH stretching modes. These results agree reasonably with the experimental frequencies of bending, 1670 cm^{-1}, and stretching, 3557 cm^{-1} (Falk & Walley, 1961). MD simulation reproduces correctly the shape of the density profile. As expected the sharper maximum, with the half-width about 200 cm^{-1}, has been obtained for the bending vibrations. A broader band has been found for the OH stretching. Its half-with, about 300 cm^{-1} (Hawlicka & Swiatla-Wojcik,1997), is in good agreement with the experimental half-width, about 260 cm^{-1} (Roberts et al. 2009).

MD simulations of the liquid PHH methanol yielded accurate frequencies of the basic modes; 1055 cm^{-1} for the CO stretching, 1407 cm^{-1} for the bending of the COH angle and 3342 cm^{-1} for the OH stretching. These results are in very good agreement with the experimental frequencies, 1029, 1420 and 3337 cm^{-1}, respectively (Lindgren et al, 1993).

Addition of electrolytes does not affect the CO stretching mode of methanol and their influence on bending modes, of methanol COH and water HOH, is minor (Stangret &

Gampe, 2002). Only stretching OH vibrations of water and methanol are very sensitive to the local environment of the molecules. These modes have been used to investigate the ionic solvation. The experimental spectra are composed, however, of several components. Even in the diluted solution of the electrolyte three components of the OH band must be considered: vibrations of molecules coordinated by cations and anions, as well as the vibrations of the bulk molecules. In concentrated solutions the spectra become more complex, because a solvent shared ion pair cannot be neglected. Therefore it is difficult to interpret the experimental spectra and to deduce the contributions of the anions and cations without additional assumptions. The MD simulation may provide additional information, because the frequency of the OH stretching can be computed independently for the solvent molecules in the ion coordination shells.

Density profiles of the OH stretching bands of water and methanol in the coordination shells of the ions in aqueous and methanolic solutions are displayed in Figure 9. For comparison the OH bands computed for pure water and pure methanol are also shown.
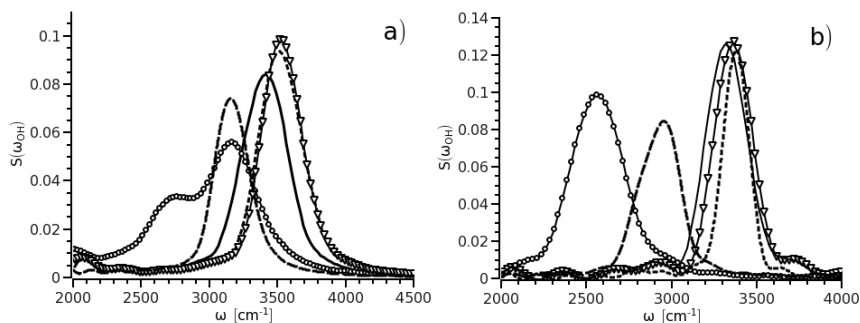

Fig. 9. Density profile of the OH stretching band of water (a) and methanol (b) in net solvents (∇) and coordination shells of Na^+ (solid), Mg^{2+} (dashed), Ca^{2+}(**O**) and Cl^- (dotted).

As seen the influence of the Cl^- ion on the OH frequency of water and methanol is minor. Despite almost linear H-bond between the anion and water molecule the red-shift of the OH frequency, observed for the water molecules in the Cl^- shell, is minor ($\Delta\omega_{OHw}$ = -27 cm^{-1}). Moreover the influence of the Cl^- ion on the OH frequency of the methanol is opposite and a small blue-shift ($\Delta\omega$= +25 cm^{-1}) is found.

The influence of the cations on the OH vibrations of the water and methanol molecules is remarkable. The frequencies of the OH stretching of the water and methanol molecules in the cation shells are shifted to lower wave numbers. This agrees with the red-shift of the molecules in the cation shells, deduced from experimental infrared spectra in HDO (Kristiansson & Lindgren, 1995; Roberts et al., 2009) . As seen from Figure 9 the OH bands of water molecules in the Na^+ and Mg^{2+} shells are broader than in pure water and the basic modes are shifted to lower wave numbers by – 125 and 265 cm^{-1}, respectively. Usually the broad OH mode, observed in pure water, is ascribed to large distribution of the configurations of the H-bonds (Lindgren et al, 1993).

The change of the OH band of the water molecules coordinated by the calcium ions is dramatic. The OH density profile is very broad; moreover it consists of two bands, centred at 3200 and 2740 cm^{-1}, respectively. As mentioned above the water molecules in the Ca^{2+} shell show two different orientations: most of 10 water molecules in the Ca^{2+} shell exhibit the antidipole orientation, but the dipole moment of some molecules is tilted by about 45°. Probably the split of the OH band reflects the vibrations of the water molecules differently orientated towards Ca^{2+}.

The cation field affects remarkably the stretching OH of the methanol molecules. The OH stretching bands, computed for the cation shells, are broader than that in pure methanol and shifted to lower frequencies. The red-shifts increases in order Na^+ (–57cm^{-1}) > Mg^{2+} (–432cm^{-1}) > Ca^{2+}(-800 cm^{-1}). One should notice that the OH band for the Ca^{2+} shell is not split, because all methanol molecules prefer similar orientation (see Figure 6 c).

The water and methanol molecules, coordinated by the cations, favoured the antidipole orientation towards the ion therefore they form less H-bonds than the molecules in net liquid component. This means that in aqueous solution about 14% of the water molecules in the Na^+ shell, more than 40% of the molecules in the Mg^{2+} shell and about 80% of molecules in the and Ca^{2+}shell have one non-bonded OH group. In methanolic solutions most of the molecules coordinated by the cations have also non-bonded OH group. The frequencies of the non-bonded OH groups of water and methanol are higher. Thus the observed red-shift of the OH frequency of the molecules coordinated by the cations is usually ascribed to the strengthening of the H-bonds (Lindgren et al, 1993; Stangret & Gampe, 2002; Kristiansson & Lindgren, 1995). This might be the consequence of a polarisation (Collahan et al. 2010) of the solvent molecules.

The BJH water and PHH methanol molecules are flexible thus their geometry and, in consequence, their dipole moments can be changed. Indeed the dipole moments of the water and methanol molecules coordinated by the cations are greater of about 10% than that of the molecules in the net solvents. However the increase of the dipole moment does not influence remarkably the H-bond energy. The Na^+ filed does not influence the H-bond energy, whereas the field of Ca^{2+} and Mg^{2+} lowers the H-bond energy, but this decrease, by about 20%, thus it cannot be responsible for the large red-shifts observed in MD simulation.

9. Conclusions

MD simulations of the electrolyte solutions improve the understanding of a nature of the solvation in methanol-water mixtures. Despite very similar interactions of the ions with both solvent components the compositions of the ion shells and the bulk solvent may be different. This leads to the conclusion that the solvation of ions does not depend only on the ion-solvent interactions, but it is affected by the interactions between the solvent molecules. Particularly in highly associated solvents a strong tendency to prevent the H-bonded network of the solvent competes with the ion-solvent interactions and it may lead to a selective solvation of the ions.

The H-bonds between the H-donor water and H-acceptor methanol molecules are energetically favourable. The molecules in the cationic shells exhibit the antidipole orientation, which favours the H-donor water molecules, whereas the almost linear H-bond

between the Cl⁻ ions and the solvent molecules favours the H-acceptor methanol molecules. In consequence the preferential hydration of the Mg^{2+} and Ca^{2+} ions and the selective solvation of Cl⁻ by methanol are observed over the whole range of the methanol concentration.

The first coordination shells of Mg^{2+} and Ca^{2+} are very stable. Though the residence time of the solvent molecules in the cationic shells is long their H-bonds are short living. It is worthy to notice than most of the molecules in the cation shells have less H-bonded neighbours than expected. Moreover the influence of the ionic field on the H-bond strength is minor. Therefore the observed red-shift of the OH-stretching frequency for water and methanol molecules reflects neither the strengthening nor stabilizing of the H-bonds. This red-shift results probably from the increase of the dipole moment of the solvent molecules.

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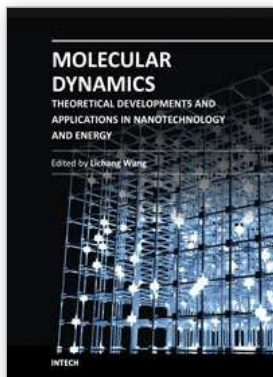
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