

Molecular Dynamics Study of CaCl_2 in Methanol

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The effective potential to describe interactions between the calcium ion and methanol molecule was derived from a potential energy surface. The energy surface was constructed from more than 10 000 points obtained from *ab initio* calculations, performed at the MP2/6-31G(d,p) level using Gaussian98. The derived effective potential and the Palinkas–Hawlicka–Heinzinger methanol model were employed in the molecular dynamics (MD) simulation of 0.25 M CaCl_2 solution in methanol at 298 K. Average distances between ions and the methanol sites—oxygen and carbon atoms—obtained from MD simulation agreed excellently with the X-ray data. The coordination number of the cation, greater as compared with the experimental results, is in accord with its concentration dependence.

1. Introduction

Our attention is focused on hydration of calcium ions in aqueous alcohols. The Ca^{2+} ion, similar to other physiological ions, is essential for the biological activity of many polyelectrolytes, such as heparin, dextran, and polynucleotides.¹ The biological activity of such polyelectrolytes is affected by a binding of the metal ions, and that phenomenon is probably dependent on an ion hydration.² Interaction of the hydrated ions with the polyelectrolyte is mostly electrostatic, and the ions, bound territorially, can move freely around the polyelectrolyte chain. A stronger and specific binding is expected for either bare or partially dehydrated ions.

Self-diffusion studies³ have shown that the addition of small amounts of methanol to diluted aqueous solution of CaCl_2 causes a decrease in the hydrodynamic radius of Ca^{2+} . The smallest Ca^{2+} radius has been observed in mixed solvent containing 10 mol % methanol. Afterward the radius increases with the increasing methanol content. Such behavior suggests size changes and may be dependent on the composition of the Ca^{2+} coordination shell.

Though X-ray and neutron scattering experiments provide direct insight into the coordination shell of the ions, their results may be not decisive, particularly for complex systems such as solutions of electrolytes in methanol–water mixtures. Distances of the Ca^{2+} ions, similar to those of other metal cations, and the oxygen atom in water⁴ and methanol⁵ are very close. Interactions between the metal ions and carbon atoms are rather weak; therefore, there is lacking a direct correlation of Ca^{2+} and other metal ions with the carbon atom of the methanol molecule. In consequence, the observed Ca^{2+} –C peak is broad and poorly defined. Moreover, this peak overlaps with maxima due to interactions of the oxygen atoms with the carbon atom as well as with a chloride ion.^{4,5} It is worth mentioning that the scattering experiments require rather high salt concentration, above 1 M, much higher than the concentration applied in experiments with polyelectrolytes. Thus molecular dynamics (MD) simulation might be a useful tool for providing additional information about the size and composition of the ion coordination shell.

Solutions of CaCl_2 in aqueous methanol have been simulated previously.⁶ We employed potentials of the Lennard-Jones type

to describe interactions of the ions. The results were, however, astonishing. They have shown a strong effect of the methanol addition on the composition of the Ca^{2+} coordination shell. In consequence, the number of the methanol molecules in the Ca^{2+} shells was markedly larger than the number of water molecules and the methanol content in the cation vicinity was much higher compared with that in the bulk solution. These results suggested an aggregation of the methanol molecules around the calcium ions, which can become a nucleus of a phase separation.

Such a feature was unexpected. The binding energy per solvent molecule in the $\text{Ca}^{2+}(\text{CH}_3\text{OH})_n$ clusters is only slightly lower compared with that in $\text{Ca}^{2+}(\text{H}_2\text{O})_n$ complexes. That small difference cannot result in the strong preferential solvation of the Ca^{2+} ions by the methanol molecules. Moreover, these MD results were inconsistent with those of the self-diffusion experiments. The aggregation of the methanol molecules around the Ca^{2+} ions would retard strongly methanol translations. In consequence, the methanol self-diffusion coefficient would be significantly reduced. Experiments³ did not show any noticeable influence of the calcium chloride on the methanol self-diffusion coefficient. Self-diffusion experiments excluded also the association of the opposite ions, whereas according to the MD results both solvent-separated and contact ion pairs are formed even in aqueous methanol.

We have noticed previously⁷ that potentials of the Lennard-Jones type considerably underestimate dynamic properties of the simulated systems. This was also a case of the CaCl_2 solutions in the methanol–water mixtures. The residence time of the solvent molecules in the coordination shells of the Ca^{2+} ions was about 30 ps.⁸ That time is comparable with the characteristic time of the cation translations, estimated from the self-diffusion coefficient, which means that the shell is rather unstable and motions of the cation and its coordination shell are independent. The hydrodynamic radius of Ca^{2+} significantly exceeds its crystal radius, which indicates that motions of the cation and at least molecules forming its first coordination shell must be strongly correlated. Therefore, the lifetime of the first coordination shell of Ca^{2+} should be similar to or even longer than that of the Na^+ shell, about 180 ps.⁹

Such large discrepancies between the results of experiments and MD simulation confirm the previous supposition that the

TABLE 1: Parameters Q_{ij} , A_{ij} , B_{ij} , and C_{ij} for Interactions of Ion–Methanol and Ion–Ion

i	j	Q_{ij} [kJ Å mol ⁻¹]	A_{ij} [kJ Å ⁿ mol ⁻¹]	B_{ij} [kJ mol ⁻¹]	C_{ij} [Å ⁻¹]	n	ref
Ca	O	-1667.3	-1372.6	2.5970×10^5	3.4900	2	this work
Ca	H	972.58	933.29	8.3273×10^2	0.9600	2	this work
Ca	Me	694.70	-474.93	5.1660×10^4	2.7930	2	this work
Cl	O	833.61	127.00	1.4529×10^5	3.1999	2	10
Cl	H	-486.27	-193.37	2.5086×10^4	3.3082	2	10
Cl	Me	-347.34	6.7657	5.9250×10^5	3.2984	2	10
Ca	Ca	5557.6	-15198	2.6010×10^6	4.4870	6	this work
Cl	Cl	1389.4	-28672	9.1704×10^5	3.3863	6	15
Ca	Cl	2778.8	-353.01	3.6608×10^5	3.0100	2	4

potentials of the Lennard-Jones type represent the ion interactions incorrectly. That stimulates us to elaborate new pair potentials for interactions of calcium chloride in methanol–water mixtures.

The pair potentials, describing interactions of the chloride ions with methanol¹⁰ and water,¹¹ were derived previously via ab initio calculations on the Hartree–Fock level. They were used to simulate NaCl solutions in methanol–water mixtures. Structural^{10,11} and dynamic⁹ results of these simulations are in very good agreement with the experimental data. In such a case these pair potentials can be also used to represent chloride ions in methanol–water solutions of CaCl₂.

Pair potentials for the calcium ions in aqueous solution were elaborated in similar way via ab initio calculations on the Hartree–Fock level.⁴ The agreement between structural results of MD simulation and X-ray experiments for aqueous solution has been very satisfactory;⁴ thus these potentials can be applied for the CaCl₂ solutions in the methanol–water mixtures. There is, however, a lack of similar pair potentials for interactions of the calcium ion and methanol. Thus the aim of the present work was to elaborate effective pair potentials for the Ca²⁺ ion and the methanol molecule, modeled as a flexible three-site body.

2. Effective Potential for Calcium Ion–Methanol Interactions and Details of the Simulation

An effective potential for calcium ion–methanol interactions was derived from energies of Ca²⁺–CH₃OH complexes obtained from ab initio calculations. A potential surface was calculated by moving a Ca²⁺ ion around a single methanol molecule. The methanol geometry was kept fixed during this procedure. The potential surface was constructed from more than 10 000 points. The calculations were performed at the MP2/6-31G(d,p) level using Gaussian98.¹²

An effective potential of the calcium ion and the methanol molecule interactions was obtained by fitting the potential energy surface for the ion–methanol complexes to the following analytical form:

$$V_{ij}(r) = \sum_{j=1}^3 \left[\frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{n_{ij}}} + B_{ij} \exp(-C_{ij}r_{ij}) \right] \quad (1)$$

where r_{ij} denotes distance between the ion and the sites of the methanol molecule. The methanol molecule was represented by three interacting sites: oxygen, hydroxyl hydrogen, and methyl group.

Q_{ij} terms represent the Coulomb interactions, which are defined by the partial charges of the three sites of the Palinkas–Hawlicka–Heinzinger (PHH)¹³ methanol molecule. The energies of Coulomb interactions were subtracted from the potential surface. In the fitting procedure multipole exponents n_{ij} were assumed to be 2, similar to the values for other ion–solvent effective potentials, e.g., for Ca²⁺ and water⁴ and for Cl⁻ and

water¹¹ and methanol.¹⁰ Parameters A_{ij} , B_{ij} , and C_{ij} , which have no physical meaning, were adjusted to the non-Coulomb part of the energy surface. The final parameters are summarized in Table 1. A comparison of the ab initio energy points and the fitted potential for an anti-dipole orientation of the methanol molecule toward the calcium ion is shown in Figure 1. For this selected orientation the minimum of the fitted curve, at 0.230 ± 0.005 nm, coincides with the minimum of the potential energy obtained from the ab initio calculations. The ab initio minimum is slightly deeper and discrepancies, less than 5%, result from the fact that the very simple functions must describe the interactions between Ca²⁺ and the methanol molecule for all methanol orientations.

To verify the fitted Ca²⁺–methanol potential and check an influence of the basis set on the fitted parameters, we have constructed the potential surface for the Ca²⁺–H₂O complexes at the same MP2/6-31G(d,p) level and compared this energy surface with the effective Ca²⁺–water potential elaborated previously by Probst et al.⁴ As mentioned above, this effective potential was derived from the energy surface obtained for a different basis set. Points obtained from our ab initio calculations for the anti-dipole orientation of the water toward Ca²⁺ are compared in Figure 2 with the effective Ca²⁺–water potential derived by Probst et al.⁴

As seen from Figure 2, the previously derived parameters reproduce our ab initio calculations fairly well: the minimum of the curve coincides with the minimum of the potential energy obtained from the ab initio calculations at 0.235 ± 0.005 nm and the discrepancies between both energies are less than 5%.

For the Ca²⁺–CH₃OH and Ca²⁺–H₂O complexes the positions of the global energy minimum are the same, within statistical error. In the global minimum the binding energies of Ca²⁺ with both solvents are very close and equal -244 and -252 kJ·mol⁻¹ for methanol and water, respectively. A similar

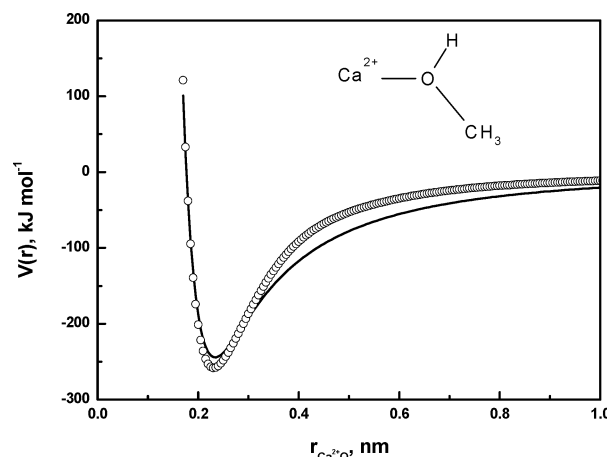


Figure 1. Effective Ca²⁺–methanol potential (solid line) for the anti-dipole orientation shown in the inset. Points (○) represent energies from the ab initio calculations.

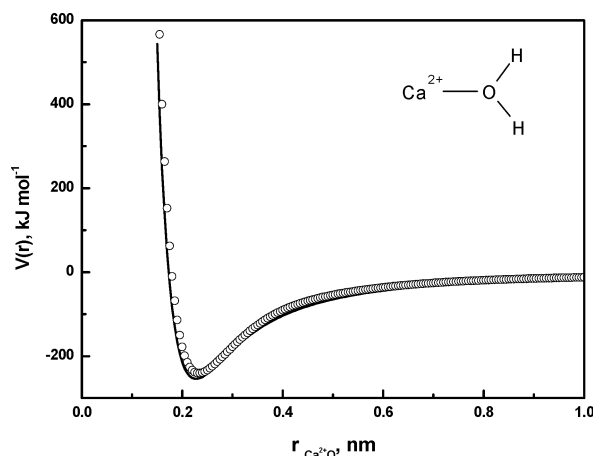


Figure 2. Comparison of potential energies of Ca^{2+} –water complexes from ab initio calculations (○) with the effective potential derived by Probst et al.⁴ (solid line) for the anti-dipole orientation (see the inset).

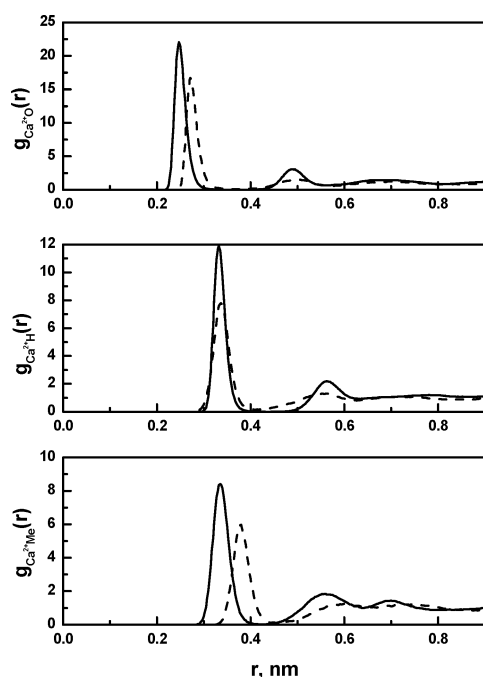


Figure 3. Ca^{2+} –methanol oxygen (top), Ca^{2+} –methanol hydrogen (middle), and Ca^{2+} –methyl group (bottom) radial distribution functions for the derived effective potential (solid lines) and the Lennard-Jones type of the potential (dashed lines).

feature has been found previously for the binding energies of the Na^+ complexes with methanol and water.¹¹

MD simulations of the CaCl_2 solution in methanol were performed using the PHH¹³ flexible model of the methanol molecule and the newly derived effective potential for interactions between Ca^{2+} and methanol. Interactions between Cl^- and methanol molecules were represented by the effective potential elaborated by Marx et al.,¹⁰ whereas for ion interactions we used effective potentials elaborated previously by Probst et al.⁴ and Dietz et al.¹⁵ All these potential parameters are summarized in Table 1.

MD simulations were carried out at 298 K for a microcanonical NVE ensemble. Methanol molecules were described by the PHH model.¹³ The concentration of CaCl_2 was equal to 0.25 M. Thus the periodic cube contained 400 methanol molecules, four cations, and eight anions. Its length, calculated from experimental density, $d = 0.81871 \text{ g}\cdot\text{cm}^{-3}$ at 298 K, was 2.996 nm. We simulated the same solution using the potentials

TABLE 2: Characteristic Parameters of the Radial Distribution Functions: Positions (in nm) of Maxima R_{max} and Minima r_{min} , the First Maximum Height $g(R_{1\text{max}})$, and Coordination Numbers n_{M}

ion	site	$R_{1\text{max}}$	$g(R_{1\text{max}})$	$r_{1\text{min}}$	$n_{\text{M}}(r_{1\text{min}})$	$R_{2\text{max}}$	$n_{\text{M}}(r_{2\text{min}})$
Ca^{2+}	O	0.247	22.03	0.367	7.6(4)	~0.49	9.5
		0.272	16.76	0.374	7.0(2)	0.497	7.1
	H	0.332	11.90	0.437	7.6(4)	0.562	11.1
		0.337	7.80	0.412	7.0(4)	0.552	9.0
	CH ₃	0.335	8.41	0.424	7.6(4)	0.560	13.0
Cl^-	O	0.380	5.98	0.450	6.9(6)		
		0.327	7.27	0.416	7.0(2)	0.560	9.5
	H	0.370	3.29	0.460	6.0(0)	0.555	10.9
		0.232	13.48	0.340	7.0(0)	~0.47	8.8
		0.277	4.34	~0.36	4.0(5)		

of the Lennard-Jones type for all interactions involving ions. Details of these potentials have been presented previously.⁶

In both simulations the same initial configurations, obtained by random placement of particles in the cubic box, were used. Ewald summation was applied for Coulomb interactions, and the shifted force potential method was used for all non-Coulomb ones.¹⁶ The simulation time step was 0.25 fs. After about 7.5 ps of equilibration, simulations of systems were extended up to 150 and 50 ps for the new fitted potential and the Lennard-Jones type of potential, respectively. Velocities and coordinates of all sites were collected in 1 fs intervals for the first 50 ps and in 10 fs intervals for the rest of simulation. In both simulations, the stability of the potential energy was better than 0.1%.

3. Results and Discussion

Radial Distribution Functions of Ions. The nearest surrounding of the calcium ion in methanol solution is described by three radial distribution functions (O, H, and CH₃). These radial distribution functions are shown in Figure 3, and their characteristic parameters (positions of the first maximum $R_{1\text{max}}$ and the second maximum $R_{2\text{max}}$, the height of the first maximum $g_{ij}(R_{1\text{max}})$, and positions of the first minimum $r_{1\text{min}}$) are listed in Table 2. Numbers of the methanol molecules in the first $n_{\text{M}}(r_{1\text{min}})$ and second $n_{\text{M}}(r_{2\text{min}})$ coordination shells were calculated by integration of the $g_{ij}(r)$ function up to the first and second minima, respectively:

$$n_{\text{M}} = 4\pi\rho_{\text{M}}\int_0^{r_{1\text{min}}} g_{ij}(r)r^2 dr \quad (2)$$

where ρ_{M} is the number density of the methanol. These results are also summarized in Table 2. For comparison the characteristic parameters obtained for the Lennard-Jones type of potentials are given in italics.

As seen from Figure 3 the Ca^{2+} –O radial distribution function exhibits two peaks. The position of the first maximum at $0.247 \pm 0.002 \text{ nm}$ is in excellent agreement with the cation–oxygen distance $0.239 \pm 0.019 \text{ nm}$ deduced from the X-ray diffraction experiments.⁵ The difference between the experimental data and the simulation result, about 4%, is less than the experimental error. The average distances between Ca^{2+} and oxygen in methanol solution is very close to that obtained for aqueous solutions: 0.239 nm from MD simulation⁴ and 0.246 nm from X-ray diffraction.^{5,17}

The number of methanol molecules in the first coordination shell is 7.6. This means that the first coordination shell of the calcium ion consists of either 7 or 8 methanol molecules. Thus the number of the methanol molecules in the first coordination shell of Ca^{2+} is smaller than its hydration number, 9.2, obtained

in MD simulation for very a similar cation–water potential.⁴ Such a feature agrees with the results of X-ray experiments, which have shown that the Ca^{2+} ion coordinates fewer methanol than water molecules.

The coordination number of Ca^{2+} obtained in recent X-ray diffraction studies⁵ is smaller compared with the MD results. The experiments show, however, that the coordination number in aqueous and methanol solutions decreases with increasing salt concentration. In methanol the calcium ion is six-coordinated for 1 M CaCl_2 solution and becomes five-coordinated when the salt concentration increases up to 2 M. The concentration of the simulated solution is lower, 0.25 M; thus the greater coordination number fits the tendency observed in X-ray experiments. Moreover, the X-ray experiments have shown that this method “is not sensitive enough to decide the coordination number of calcium ion with high precision”.⁵

The height of the $g_{\text{CaO}}(r)$ first peak, about 22, coincides with the values 23.8 and 18.54 observed in 1 and 0.05 M solutions.¹⁸ In methanol the $g_{\text{CaO}}(r)$ peak is about 2 times higher than that in aqueous solution;⁴ these heights are 22 and 14, respectively. Similar differences were observed previously for other ions.^{7,11} Because the calcium ion coordinates fewer methanol than water molecules, the increase of the peak height must reflect a more restricted location of the methanol molecules around the calcium ion.

The second solvation shell of Ca^{2+} is represented by a broad peak of the $g_{\text{CaO}}(r)$ function, located between 0.46 and 0.52 nm. The position of the second maximum coincides with a very broad peak, centered at about 0.46 nm, observed in the X-ray experiments.⁵ The Ca^{2+} second shell contains only nine methanol molecules (see Table 2). A larger shell, consisting of more than 11 or even more than 15 methanol molecules, has been found in X-ray experiments⁵ and MD simulation,¹⁸ respectively. The data extracted from X-ray results do not seem to be very accurate, because the peak ascribed to the Ca^{2+} second shell overlaps a peak of two carbon atoms.⁵ The distance between the oxygen atoms in the first and second shells of Ca^{2+} is very short, only about 0.22 nm, much shorter than the distance between two H-bonded methanol molecules. Moreover, the number of methanol molecules in the second shell higher than 11 suggests that almost all methanol molecules in the first Ca^{2+} shell have two neighbors. Such feature does not agree with the anti-dipole orientation of the methanol molecules in the first coordination shell.

As seen from Figure 3, the $g_{\text{CaO}}(r)$ function obtained for the LJ type of potential exhibits two peaks: the first at 0.27 nm and a very poorly defined second peak about 0.5 nm. Thus the average distance between the Ca^{2+} ions and the oxygen atoms of the nearest neighbors is longer compared with the experimental results. This confirms previous observations⁷ that the LJ potential overestimates average distances between the ion and solvent sites as a result of underestimating the ion–solvent interactions. The integration of the first $g_{\text{CaO}}(r)$ maximum yields a slightly smaller coordination number, $n = 7$.

The $g_{\text{CaH}}(r)$ function, shown in Figure 3, exhibits a sharp maximum at 0.332 ± 0.002 nm. The integration of that peak yields $n = 7.6$, which confirms that the calcium ion coordinates either seven or eight methanol molecules. Compared with the $g_{\text{CaO}}(r)$ function, the first peak of the $g_{\text{CaH}}(r)$ function is shifted to longer distance by about 0.085 nm. Although that difference is slightly larger compared with that for the $g_{\text{CaO}}(r)$ and $g_{\text{CaH}}(r)$ functions in aqueous solution (0.074 nm),⁴ it suggests that an anti-dipole orientation of the methanol molecules in the first coordination shell of Ca^{2+} is very probable.

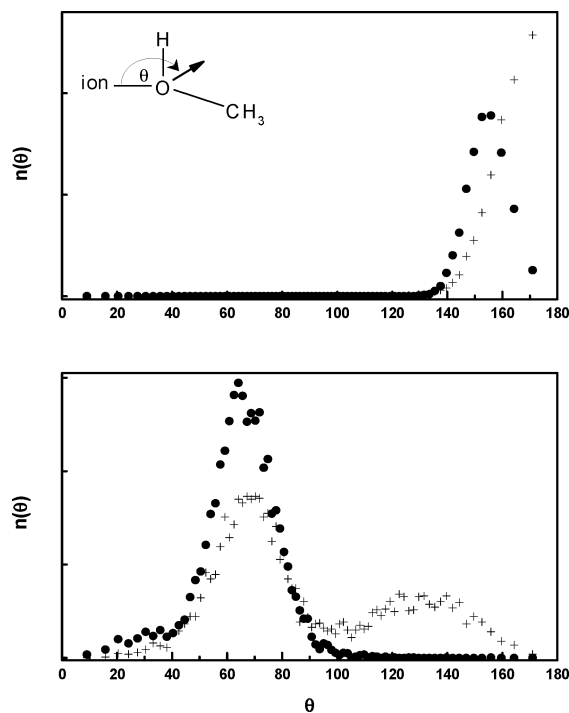


Figure 4. Angular distribution functions of the nearest methanol molecules around Ca^{2+} (top) and Cl^- (bottom) for the effective potentials (●) and Lennard-Jones potentials (+). θ is the angle between the dipole moment of the methanol molecule and the vector connecting the ion and oxygen (see the inset).

The orientation of the solvent molecules around ions is characterized by an angle between the vector connecting the ion with the oxygen and the dipole moment of the methanol molecule. The distribution of that angle, θ , presented in Figure 4, exhibits a maximum at $\theta \sim 155^\circ$. Thus the dipole moments of the nearest methanol molecules are tilted by about 25° from the anti-dipole arrangement. This makes a difference between the coordination shells in methanol and aqueous solutions. In aqueous solution the nearest neighbors exhibit almost strict anti-dipole orientation⁴ and only the dipole moment of one water neighbor is tilted by about 55° from the anti-dipole orientation.

The $g_{\text{CaMe}}(r)$ function (see Figure 3) shows a sharp maximum located at 0.335 ± 0.002 nm. The integration of that peak yields $n = 7.3$, confirming that Ca^{2+} coordinates at least 7 methanol molecules. The position of the $g_{\text{CaMe}}(r)$ maximum is in very good agreement with the Ca^{2+} –carbon distance (0.352 ± 0.020 nm) extracted from the experimental data.⁵

The $g_{\text{ClO}}(r)$ and $g_{\text{ClH}}(r)$ radial distribution functions are shown in Figure 5, and their characteristic parameters are summarized in Table 2. A sharp peak of the $g_{\text{ClO}}(r)$ function is found at 0.327 ± 0.002 nm, at the same position, 0.33 nm, that the $g_{\text{ClO}}(r)$ maximum has been observed in NaCl solution.^{7,11} That result is very close to the average Cl–O distances estimated from X-ray experiments for MgCl_2 ¹⁴ (0.328 nm) and CaCl_2 ⁵ (0.319 ± 0.02 nm) solutions and suggests that the counterion does not affect the first coordination shell of the anion. This leads to the conclusion that the ion pair formation either does not occur or is negligible in the simulated system. That is in accord with X-ray experiments,⁵ which have shown that the contact ion pairs either are not present in 1 M CaCl_2 solution or their concentration is very low at this concentration.

As might be expected, the first maximum of the $g_{\text{ClO}}(r)$ function obtained from simulation with the LJ potentials is shifted to a larger distance, 0.370 ± 0.002 nm, similar to what has been observed previously for methanol solution of NaCl.⁷

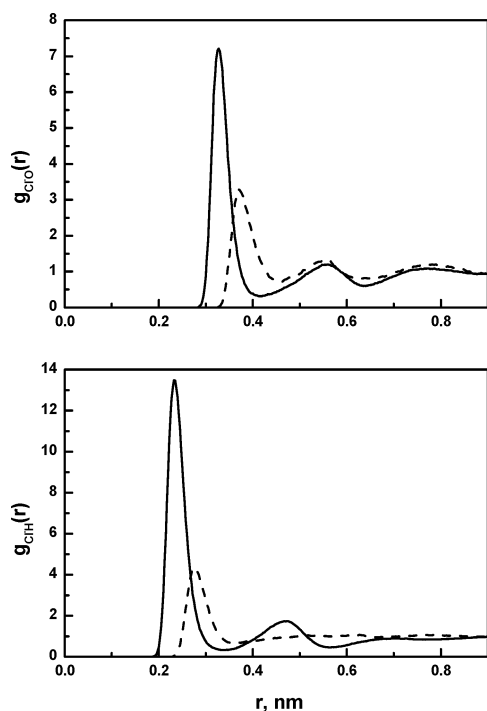


Figure 5. Cl^- –methanol oxygen (top) and Cl^- –methanol hydrogen (bottom) radial distribution functions for effective (solid lines) and Lennard-Jones (dashed lines) potentials.

This confirms that the LJ type of potentials does not reproduce accurately the solution properties.

Integration of the first $g_{\text{ClO}}(r)$ peak yields $n = 7$, similar to what has been obtained for NaCl in methanol.⁷ The X-ray experiments⁵ have shown six methanol molecules coordinated by chloride ion in the methanol solution of CaCl_2 , but more than six methanol molecules, $n = 7.7$, coordinated by Cl^- in methanol solution of MgCl_2 .¹⁷ A discrepancy between the results of MD simulation and of X-ray experiments may be due to a higher concentration of the experimentally examined solution. It is worth noticing that the minimum of the $g_{\text{ClO}}(r)$ function obtained from MD simulation is poorly defined; therefore the coordination number computed for the Cl^- ion is less certain than that of the Ca^{2+} ion. A smaller coordination number, $n = 6$, obtained in MD simulation with LJ type of potentials (see Table 2) may suggest a formation of the ion pairs.

The sharp maximum of the $g_{\text{CH}}(r)$ function is observed at 0.232 ± 0.002 nm. The average distance between the Cl^- ions and the hydroxyl hydrogen is about 0.095 nm shorter than the distance between Cl^- ions and oxygen atoms. That suggests a formation of almost linear hydrogen bonds between the anion and the methanol molecule. In fact, the angular distribution function exhibits a maximum at 64° (see Figure 4). Similar orientation of methanol molecules around the chloride anion has been observed previously.^{10,11}

Elaboration of a new effective potential to describe the interactions between the calcium ion and methanol was undertaken because the LJ type of potentials did not reproduce accurately several properties of CaCl_2 solutions in aqueous methanol. One unrealistic behavior, observed in the previous simulation, was a strong association of unlike ions, which led to the aggregation of all ions and to a phase separation.⁶ Neither the phase separation nor the association of unlike ions has been observed experimentally for salt concentration below 1 M.

As seen from Figure 6, the $g_{\text{CaCl}}(r)$ function obtained for the LJ potentials shows a sharp maximum at 0.297 ± 0.002 nm. The peak at that position has been attributed to contact ion pairs.⁵

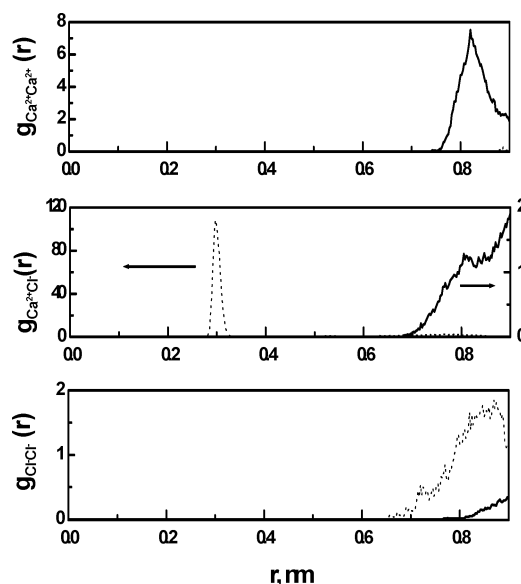


Figure 6. Radial distribution functions of ions Ca^{2+} – Ca^{2+} (top), Ca^{2+} – Cl^- (middle), and Cl^- – Cl^- (bottom) for effective (solid lines) and Lennard-Jones (dotted lines) potentials.

The contact ion pairs were observed in 2 M CaCl_2 solution in methanol, but they did not appear in less concentrated solution (1 M). Therefore, their existence in 0.25 M solution proves that the LJ potential either overestimates the interactions between ions or underestimates the ion–solvent interactions.

The newly derived potentials together with the ion–ion potentials derived in a similar way seem to reproduce the intermolecular interactions more accurately, because the Ca^{2+} – Cl^- radial distribution function, shown in Figure 6, exhibits no peak either at 0.27 nm or at 0.51 nm, i.e., at the distances attributed to either the contact or the solvent-separated ion pairs.⁵ A lack of ion pairs is consistent with the self-diffusion results, which do not confirm the association of the ions.

Residence Time of Solvent Molecules in the Coordination Shells. The residence time of the solvent molecules in the nearest neighborhood of the ions provides information on the lifetime and stability of the coordination shells.^{7,9} This residence time has been calculated from time correlation function $R(t)$:

$$R(t) = \frac{1}{n_{\text{ion}} n_{\text{M}}} \sum_{i=1}^{n_{\text{ion}}} \sum_{j=1}^{n_{\text{M}}} [\theta_{ij}(0) \theta_{ij}(t)] \quad (3)$$

where n_s is the number of methanol molecules in a sphere of the radius r defined as the position of the first minimum of the $g_{\text{ionO}}(r)$ function and n_{ion} denotes the number of ions. $\theta_{ij}(t)$ is the step function, which is 1 if the methanol molecule j has been in the coordination shell of the ion at time t and 0 otherwise; n_{M} is the number of methanol molecules in the first coordination shell (solvation number).

The calculations have been 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 molecule could leave the surrounding of the ion for a period, which was shorter than Δt ; otherwise they were neglected in further calculations. Examples of the time correlation functions $R(t)$, calculated for the different Δt values, are displayed in Figure 7.

As seen from Figure 7, variations of the time interval Δt do not influence the character of the $R(t)$ functions. These functions for Ca^{2+} ions decrease rapidly during the period shorter than 1

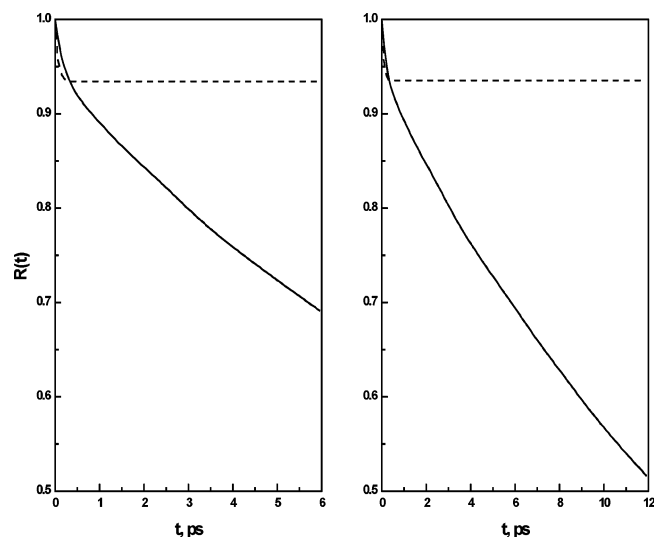


Figure 7. Time correlation functions $R(t)$ of the methanol molecules in the shells of Ca^{2+} (dashed lines) and Cl^- (solid lines), for time intervals: $\Delta t = 0.05$ ps (left) and $\Delta t = 0.10$ ps (right).

ps; afterward, independently of the time intervals, they reach a constant value close to 0.95. This means that more than 95% of the methanol molecules do not leave the coordination shell during the whole simulation time. Thus the residence time must exceed 150 ps and the coordination shell of the calcium ion is very stable. The methanol molecules stay in the Ca^{2+} shell much longer than in the Na^+ coordination shell,⁹ about 45 ps. Such a feature seems to be realistic, because an elongation of the residence time with increasing charge density is expected. In aqueous solution the lifetime of the hydration shells of Ca^{2+} is much longer compared with that of the Na^+ shells.¹⁹ Self-diffusion data for ions and solvents⁸ yield a dynamic solvation number greater than 6 for the Ca^{2+} ion. This means that the Ca^{2+} field must control translations of at least the six nearest methanol molecules. Thus motions of the ion and its nearest neighbors are strongly correlated. In such a case the residence time should significantly exceed 32 ps, i.e., the characteristic time of the ion translations.

The $R(t)$ functions for the chloride ion decrease monotonically, and their decrease depends on the time intervals. They can be fitted to a second-order exponential decay:

$$R(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_{\text{RES}}}\right) \quad (4)$$

The first term denotes the probability of an escape of the molecules located close to the border of the coordination shell. This process is rather fast with the characteristic time $\tau_1 < 1$ ps. The second term describes the stability of the ion neighborhood, and τ_{RES} is the residence time of the solvent molecule in the ion coordination shell. Parameters A_1 and A_2 reflect the percentages of the molecules involved in both processes.

An influence of the time intervals Δt on the residence time in the Cl^- coordination shell is shown in Figure 8. The τ_{RES} values increase with the increasing Δt , but when the time interval is not shorter than 0.2 ps, the variations of τ_{RES} become not significant. Thus the residence times discussed below were calculated for $\Delta t = 0.2$ ps, which means that the methanol molecules leaving the ion neighborhood for the period longer than 0.2 ps were neglected in further calculations.

Almost 92% of the methanol molecules in the nearest surrounding of Cl^- stay in the coordination shell longer than 25 ps. A similar result has been obtained previously for the

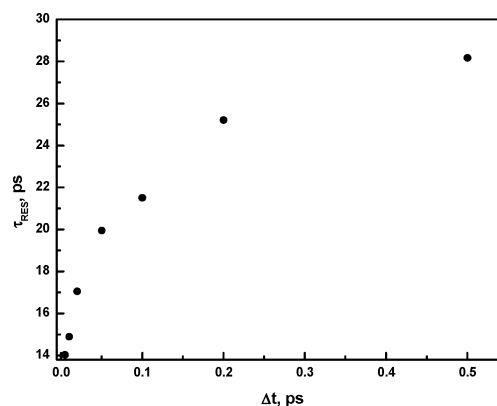


Figure 8. Dependence of residence time of methanol molecules in the coordination shell of Cl^- on the time interval Δt for the effective potential.

Cl^- ions in methanol– NaCl solution. That result coincides with the characteristic time of the chloride ion translations, about 20 ps. In methanol the hydrodynamic radius of Cl^- exceeds the radius in crystal, and its dynamic coordination number⁸ is about 3. Thus the anion field controls the translations of a few methanol neighbors, and their residence time must be either longer than or comparable to the characteristic time of the anion translations.

As might be expected, the lifetimes of the Ca^{2+} and Cl^- shells obtained from the simulation with the LJ type of the ion–solvent potentials are much shorter. About 90% of the methanol molecules stay within the Ca^{2+} coordination shell about 55 ps. Though this time is longer than 32 ps, the characteristic time of the cation translations,⁸ a much longer time is expected for two reasons. As mentioned above, the dynamic solvation number calculated from the self-diffusion data is very close to the static solvation number obtained from MD simulation and estimated from X-ray experiments. Such a feature reflects a strong correlation of the motions of the ion and its neighbors; therefore, the solvent molecules should stay in the vicinity of the ion much longer than the time needed for one jump. Moreover, the lifetime of the coordination shell increases significantly with the increasing charge density of the ion. In aqueous solution the lifetime of the Ca^{2+} shell is about 30 times longer compared with that of the Na^+ shell. Methanol molecules reside in the vicinity of the sodium ions about 45 ps; thus the residence time of about 55 ps obtained for the first coordination shell of Ca^{2+} ions is too short.

4. Conclusions

MD simulation with the effective potentials derived from ab initio calculations and fitted to the analytical form of eq 1 reproduces correctly the most important structural properties of the system. The average distances between the ions and the methanol sites, oxygen and carbon atoms, are equal, within experimental error, to the values extracted from the X-ray experiments.⁵ Though the coordination numbers of both cation and anion obtained from MD simulation are slightly larger compared with those estimated from X-ray experiments, that discrepancy could be understood, not only because the concentration of the simulated solution was about 4 times lower compared with that used in the experiments, but also because the X-ray experiments do not yield the coordination number of the calcium ion with high precision.⁵ Dipole moments of the methanol molecules around Ca^{2+} are slightly tilted from the anti-dipole orientation, whereas those in the vicinity of Cl^- ions form almost linear hydrogen bonds with the anion.

Association of the unlike ions does not occur. This is in accord with the self-diffusion experiments and X-ray results, which have shown that ion pairs appear in more concentrated solutions, above 1 M.⁵

This new effective potential of the ions and methanol better reproduces the dynamic properties of the simulated system. The lifetime of the Ca^{2+} coordination shell is long, much longer than the lifetime of the Cl^- shell and the characteristic time of the ion translation. Such a feature agrees with the results of the self-diffusion experiments.³

Satisfying agreement of the MD simulation results with the results of X-ray and self-diffusion experiments leads us to believe that the newly elaborated effective potential describes interactions between the calcium ion and the methanol molecule correctly. Thus it can be used in further MD simulations of the CaCl_2 solutions in methanol–water mixtures. Such simulations may give insight into changes of the Ca^{2+} coordination shells with the solvent composition.

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