



Influence of ions on molecular vibrations and hydrogen bonds in methanol–water mixtures MD simulation study



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ABSTRACT

Solutions of NaCl, MgCl₂ and CaCl₂ in methanol–water mixtures have been investigated by the molecular dynamics simulations. Special attention has been paid to the OH stretching frequencies and hydrogen bonds of the water and methanol molecules in the subsystems; the coordination shells of the ions and the bulk solvent. The influence of the ions on the properties of the solvent molecules is limited to the first coordination shells and it depends on the ion charge density. Thus all cations affect the intramolecular bonds, valence angles, and the dipole moment and the Cl[−] ion influences only the length and vibrations of the nearest OH bond of the water molecules, but it does not affect the properties of the methanol molecules. Though the influence of the cations on the solvent molecules is strong, the interactions between the solvent molecules enhance the molecular polarization. In consequence the induced dipole moment and the OH frequencies of the water and methanol molecules in the cation shells depend also on the methanol mole fraction. The shift of the OH stretching frequency correlates linearly with the induced dipole moment, but it does not correlate with the strength of the hydrogen bonds.

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1. Introduction

Alkali earth ions, Ca²⁺ and Mg²⁺, the most abundant divalent cations within cells [1], play a key role in many biochemical processes [1–3], which occur in the presence of hydrophilic and hydrophobic groups [4]. A biochemical activity of the Ca²⁺ and Mg²⁺ ions requires their partial or even complete dehydration. This accounts for a great interest in the hydration of these cations in systems, which contain the hydrophobic groups. Methanol–water mixture is such a system; therefore it is often used to investigate the ion hydration in the presence of the hydrophobic groups.

Ab initio calculations have shown [5–8] that energies of the interaction of the ions with both solvent components, water and methanol, do not differ substantially. Diffractions of X-ray [9,10] and neutron [11,12] confirmed this similarity. These experiments showed that the average distances from the cations to oxygens, either water or methanol are the same, therefore the ion–oxygen distance is independent of the composition of the methanol–water mixture [12]. Diffusion experiments [13,14] and MD simulations [15–17] have shown however that despite similar interactions of the alkali earth cations with water and methanol these ions are preferentially hydrated, even in methanol rich mixture.

The methanol–water mixture is non-homogeneous [18–20] thus the preferential hydration of the cations may preserve the hydrogen bonded networks.

Diffraction experiments [20–25] have shown that the high pressure and the salt addition affect the water structure similarly. The influence of the ions is probably more complex, because some of them (chaotropes) may destroy the water structure, whereas others (kosmotropes) may order the nearest water molecules, breaking some of the hydrogen bonds beyond the coordination shells.

IR and Raman experiments are commonly used to investigate the influence of the ions on the H-bonded network, because intramolecular motions, particularly the OH stretching vibrations, are very sensitive to a local environment of the water molecule [26] and the OH frequency correlates with the length and strength of the hydrogen bonds [27]. Usually the IR spectra were recorded for electrolyte solutions of a moderate concentration, above 0.5 M. Thus their interpretation may be difficult, because the shells of the opposite ions may overlap [28,29]. It is worthy to stress that the ionic pairs were observed above 0.1 M even in the aqueous solution of the alkali metal halides [29]. It is probably the reason that conclusions drawn from the IR spectra might be inconsistent even for the aqueous solutions of alkali metal halides.

A strong influence of the halide anions and a lack of the cation effect on the OH stretching vibrations of water [30–34] are a generally accepted picture. This assumes that the halide anions may strongly affect the OH frequency, because they form the hydrogen bonds with the water

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molecules. The influence of the cations is weaker, because their influence is indirect *via* a polarization of the coordinated molecules. This may affect the hydrogen bonds between the coordination shell and the bulk solvent. The polarization influences the length of the intramolecular OH bond and this affects the OH stretching frequency [32–35]. Such interpretation of the IR spectra, recorded for the aqueous solutions of the alkali halides, can be also found [35,36]. For aqueous solutions of alkali metal halides both the influence of the ionic pairs [37–39] as well as a lack of any influence [40,41] on the water vibrations have been noticed.

Molecular dynamic simulations may provide useful information about the influence of the ions on the molecular vibrations. The advantage of MD simulation is that the properties of interest can be calculated separately for the subsystems, such as the ionic shells and the bulk solvent. Such separation is not possible from experiments. Another advantage of the computer simulation is that the properties, which are not directly accessible from the experiments, can be also calculated.

The goal of our work was to investigate an interrelation between changes of the OH stretching frequency, the strength and stability of the hydrogen bonds and the polarization of the molecules in the coordination shells of the ions. We were also interested what causes the frequency shift for the molecules affected by the ions, particularly cations. Does the frequency shift reflect a strengthening of the hydrogen bonds of the coordinated molecules? We were interested also whether the influence of ions is extended beyond their coordination shells.

We calculated separately the frequencies of the OH stretching vibrations of the molecules in the ionic shells and the bulk solvent. Moreover we computed the properties, which are not directly accessible from the experiments: the length of the intramolecular bonds and the valence angles; and the energy and the lifetime of the hydrogen bonds. All properties of water and methanol molecules, i.e. the OH stretching frequencies, the dipole moments and the H-bond energy and lifetime were calculated separately for three subsystems, the ionic shells and the bulk solvent.

2. Potential models

Water and methanol molecules were treated as flexible three site bodies. BJH [42] and PHH [43] potentials, which were used to represent the interactions of the water and methanol molecules, respectively, consisted of the inter- and intramolecular parts. The intermolecular potentials contained the Coulomb and non-Coulomb terms. The Coulomb part resulted from the partial charges, which were located on the oxygen (−0.66 e) and hydrogens (+0.33 e) of the water molecule, and on the oxygen (−0.6 e), the hydroxyl hydrogen (+0.35 e) and the methyl group (+0.25 e) of the methanol molecule. The non-Coulomb terms were the modified CF potentials for water [44]. The same terms were used to describe the O–O, O–H and H–H non-Coulomb interactions of the methanol and water molecules. The non-Coulomb interaction of the methyl group with the hydroxyl hydrogens of water and methanol was neglected, whereas those with the other sites of the water and methanol molecules were represented by the Lennard–Jones type potential [45]. The intramolecular terms were the spectroscopic type potentials in the form as proposed by Carnet et al. [46].

$$V_{\text{intra}} = \sum L_{ij}\rho_i\rho_j + \sum L_{ijk}\rho_i\rho_j\rho_k + \sum L_{ijkl}\rho_i\rho_j\rho_k\rho_l \quad (1)$$

where ρ was a dimensionless internal coordinate, as proposed by Simons [47].

Potentials for the ion–solvent interactions were derived from *ab initio* calculations [5–8,48,49]. Potential surfaces were obtained by moving the ion around the solvent molecule, either water or methanol. The potential surfaces were constructed from more than 10,000 points. The

effective potentials for the ion–solvent interactions were obtained by fitting the potential surfaces to the following analytical form:

$$V_{ij}(r) = \sum_{j=1}^3 \frac{Q_{ij}}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{n_{ij}}} + B_{ij} \times \exp(-C_{ij} \times r_{ij}) \quad (2)$$

r_{ij} represents the distance between the ion and the sites of the solvent molecule. Q_{ij} terms represent the Coulomb interactions of the ion with the partial charges of either BJH water or PHH methanol molecules. The energies of the Coulomb interactions were subtracted from the potential surfaces. Parameters A_{ij} , B_{ij} and C_{ij} were derived by fitting these non-Coulomb parts of the potential energy surfaces to the analytical forms. The A_{ij} , B_{ij} and C_{ij} parameters, which did not have any physical meaning, have been published previously [5–8,48,49]. It is worthy to stress that the potential of the ion–solvent interactions reproduced correctly the structure and dynamics of the solvation shells of the ions. The details of the ionic solvation were discussed previously for aqueous [5,6,17,48] and methanolic [7,8,17,49] solutions as well as for the methanol–water mixtures [16,17,48].

3. Details of the simulations

MD simulations were carried out using DL-POLY2 package [50] for the canonical NVT ensemble, with the periodic boundary conditions. The cubic boxes contained 3000 solvent molecules and 15 molecules of the salt, thus the salt concentration ranged from 0.16 M in aqueous solutions to 0.09 M in methanolic solutions. The box lengths were calculated from the experimental densities of these solutions at 298 K.

Ewald summation algorithm was used for all electrostatic interactions and the shifted force method was applied for the non-Coulomb interactions. The cut-off distance was equal to 1.5 nm thus it did not exceed a half of the box length. Initial configurations were obtained by a random displacement of the molecules in the cubic box. The short time step, 0.25 fs, assured a good reproduction of the internal vibrations of the molecules. After an equilibration period of 10 ps, the simulations were performed during 250 ps.

4. Results

The spectral density $S(\omega_{\text{OH}})$ of the water and methanol hydrogens was calculated *via* Fourier transform of the normalized velocity autocorrelation functions $C_{vv}(t)$:

$$S(\omega_{\text{OH}}) = \frac{2m_H c}{kT} \int_0^{\infty} C_{vv}(t) \cos(2\pi c \omega t) dt \quad (3)$$

where ω was the frequency, m_H denoted the hydrogen mass and c was the light velocity. k and T represented the Boltzmann's constant and temperature.

The normalized velocity autocorrelation function of hydrogens was defined as follows:

$$C_{vv}(t) = \frac{1}{N_t N_\alpha} \sum_{i=1}^{N_t} \sum_{j=1}^{N_H} \frac{v_j(t_i) v_j(t_i + \Delta t)}{C_{vv}(t=0)} \quad (4)$$

N_t and N_H denoted the numbers of the time averages and of the hydrogens, respectively, $v_j(t)$ was the velocity of the j hydrogen at the time t and $C_{vv}(t=0)$ represented the normalization factor.

The density profile of the OH stretching band of water and methanol was computed for the subsystems: the coordination shells of the ions and the bulk solvent. A dimension of the ionic shells was estimated from the ion–oxygen radial distribution function. These $g(r)$ functions exhibited very sharp first peaks [15–17]. Their positions agreed excellently with the average distance between the cations and oxygens of

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