



# Concentration effects on aqueous lithium chloride solutions. Molecular dynamics simulations and x-ray scattering studies



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## ARTICLE INFO

### Article history:

Received 4 January 2014

Received in revised form 10 April 2014

Accepted 18 April 2014

Available online 5 May 2014

### Keywords:

Aqueous LiCl solutions

Molecular dynamics

Structure factor

X-ray

Diffusion coefficients

## ABSTRACT

Molecular dynamics simulations have been performed on aqueous LiCl solutions over a wide range of salt concentrations, using a flexible SPC/E water model. The resulting molecular dynamics structure factors agree remarkably with recently published x-ray ones. The diffusion coefficients of both ions and water decrease with increasing salt concentration. The self-diffusion coefficients of lithium and chloride are nearly equal at higher salt concentration, showing that large clusters of ions move as an entity. The deduced reorientational correlation time for the dipole moment speeds up as the salt concentration increases, indicating the presence of an angular jump model. The dielectric constant decreases with increasing salt concentration.

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## 1. Introduction

Water is ubiquitous on the earth and in living organisms [1], it has extraordinary microscopic properties uncommon for the majority of liquids [2], a good part of which comes from intermolecular hydrogen bonding. An understanding of the orientational dynamics of water is essential in a wide range of processes, such as the rearrangement of the water hydrogen-bond network [3], the biomolecular hydration and the drag-protein recognition [4]. In most cases, water does not exist as a pure substance, but rather it contains dissolved salts. The dielectric properties of water influence the electrolyte and therefore the salvation of ions in aqueous solutions [5].

Laage and Hynes [6,7] have proposed a molecular mechanism of water reorientation which leads to the rupture and the creation of hydrogen-bonding phenomenon in concrete terms. In the diffusive model, water molecule redirection is achieved by infinitesimal steps, whereas in the extended jump model, the exchange of H-bonding, effectuated in a very short time, is realized by large amplitude angular jumps.

The ionic aqueous solutions play a central role in environmental and industrial processes like microbiology [8], and oxidation of chemical and biochemical wastes [9]. As a consequence, they have been frequently chosen as subjects of experimental and theoretical investigations. In particular  $\text{Li}^+$  and  $\text{Cl}^-$ , which are essential for biophysical systems, continue to attract a particular attention for many reasons. For example, ion lithium is, one of the most simple metal ions playing widespread and diverse roles in biological, medical, and technical application [10].

Recently [11,12], we have presented a structural analysis of aqueous LiCl solutions by combining x-ray scattering and MD simulations. In that study, as an essential point, it was shown that the ion-pairing process increases with increasing salt concentration. Simultaneously, the degree of hydrogen bonding in liquid water clearly decreases, whereas the coordination number of water in solution increases in comparison to that of the pure fluid. To get more insight on the properties of aqueous LiCl solutions, we extend in this paper our MD investigation, to study the effects of salt concentration on dynamical properties of ions and water. In addition, all the partial correlation functions and structure factors of the systems are deduced. A comparison between experimental results and theoretical ones, using a flexible SPC/E water model, is then addressed.

The outline of this paper is the following. The computational details of the MD simulations are given in Section 2. The computed structure factors, pair correlation functions, velocity autocorrelation functions, self-diffusion coefficients, reorientational correlation times and dielectric constants are determined in Section 3. The conclusion and final remarks are presented in Section 4.

## 2. Computational details

The molecular dynamics formalism was described elsewhere [13]. Only a brief outline will be given here. In all simulations, the water molecules are characterized by the flexible SPC/E potential and the ions are modeled as charged Lennard-Jones particles. The values of the potential parameters  $q_i$ ,  $\sigma_i$ , and  $\epsilon_i$  for all particles are summarized in Table 1 [14–16]. A cubic box of 256 particles including water molecules and ions is chosen, and periodic boundary conditions with minimum image convention were used. The initial configurations of water molecules

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**Table 1**

Values of Lennard-Jones and electrostatic interaction potential parameters;  $e$  represents the magnitude of electronic charge.

Atom/ion	Charge ( $e$ )	$\epsilon$ (kJ/mol)	$\sigma$ (Å)	Ref.
O	-0.8476	0.6502	3.169	[14]
H	+0.4238	0.0	0.0	[15]
Li <sup>+</sup>	+1	0.6904	1.505	[16]
Cl <sup>-</sup>	-1	0.4184	4.401	[16]

and ions are obtained by a random displacement of the particles in the box, which the length is chosen to match the experimental density. The Lorentz–Berthelot combining rules [17] are used to describe the cross-interactions, and the long-range Coulomb forces are calculated using the Ewald summation method [18]. The convergence parameter is  $\alpha = \frac{5.36}{L}$  and the maximum  $k$  in the reciprocal space is such that  $k_{\max}^2 \leq 27$ . The non-Coulomb short range interactions were truncated using a spherical cut-off distance equal to the half of the cell length. The weak coupling scheme according to Berendsen et al. [19] is applied.

We have performed a series of sufficiently long MD simulations of aqueous LiCl solutions at different salt concentrations, ranging from 0.5 to 6 m. The simulation parameters of the studied systems are reported in Table 2. The equations of motion are integrated using the Verlet Leap-Frog algorithm and the initial velocities are generated assuming a Maxwell–Boltzmann distribution.

### 3. Results and discussion

The computed densities of aqueous LiCl solutions at different concentrations are given in Table 2 together with measured ones. There is a small difference between the experimental and theoretical values. The different contributions into the total energy are also presented in Table 2. One can see that water–water interaction energy  $E(\text{H}_2\text{O}\cdots\text{H}_2\text{O})$  is increasing with an increase of the salt concentration. This effect takes place mainly due to the disruption of the hydrogen bonds. The ion–water interactions  $E(\text{Li}^+\cdots\text{H}_2\text{O})$  and  $E(\text{Cl}^-\cdots\text{H}_2\text{O})$  both become weaker upon an increase of the salt concentration. This is due to the influence of other ions on the hydrated shell. The increase of the ion–water energy is compensated by the decrease of the ion–ion energy.

In our previous studies [11] and [12], our investigations are focused on the local structure of aqueous LiCl solutions through pair correlation functions as deduced respectively from x-ray scattering and MD simulation. In that study, some simplifying hypotheses are constructed: i) All the X–H (where X = H, O, Li<sup>+</sup>, Cl<sup>-</sup>) correlations are omitted since the contribution of such interactions to the x-ray scattered intensity are weak particularly at high  $q$  values, and ii) the contribution of ion–ion interactions which occur in MD results at relatively high distances is also omitted since no signature of these interactions appears in the x-ray pair correlation functions. However, the theoretical model which we have considered in these studies and which takes into account the

more scattering element gives reasonable concordance with x-ray results. In this study, in order to show more reliability for our computational model, we calculate the intermolecular structure factors of each system as the weighted average of all partial ones:

$$S(Q) = \frac{\sum_{\alpha,\beta} c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q) S_{\alpha\beta}(Q)}{\sum_{\alpha,\beta} c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q)} \quad (1)$$

where  $c_{\alpha} = \frac{N_{\alpha}}{N}$  is the concentration of  $\alpha$  specie,  $f_{\alpha}(Q)$  is the x-ray form factor and  $S_{\alpha\beta}(Q)$  is the partial static structure factor directly deduced from MD simulation via the relation:

$$S_{\alpha\beta}(Q) = 1 + \frac{4\pi\rho_0}{Q} \int_0^{\infty} r [g_{\alpha\beta}(r) - 1] \sin(Qr) dr \quad (2)$$

where  $\rho_0$  denotes the atomic number density of the system.

In a similar way, the intermolecular pair correlation function  $g_L(r)$  of each system is the weighted average of the partial ones [13]:

$$g_L(r) = \frac{\sum_{\alpha,\beta} c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q) g_{\alpha\beta}(r)}{\sum_{\alpha,\beta} c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q)} \quad (3)$$

Fig. 1(A) shows the MD and the x-ray structure factors  $S(Q)$  for each system. It can be noted that the agreement between the calculated and experimental data is quite good. The mean feature of the experimental pair correlation function  $g(r)$  (Fig. 1(B)) is also well reproduced by the calculated ones. Particularly, calculated and experimental curves reveal a good concordance in the description of the development of the intermolecular interactions and the disruption of the water structure as a function of salt concentration.

To get an idea about the dependence of the system size on the structure factor and pair correlation functions, three different systems corresponding to  $C = 3$  m and containing respectively 256, 526 and 1052 particles were used. In Fig. 2(A), we have drawn the MD structure factor and the corresponding pair correlation function of each system. Manifestly, the oscillatory character of the curves is slightly amplified whereas the intermolecular interactions are at the same positions Fig. 2(B).

The dynamical properties of the ions and water molecules can be examined via the velocity autocorrelation functions (VACFs). The normalized VACF,  $Cv_i(t)$ , for the  $i$ th particle is defined as:

$$Cv_i(t) = \frac{\langle v_i(t) v_i(0) \rangle}{\langle v_i(0)^2 \rangle} \quad (4)$$

where  $v(t)$  is the velocity of the ion at time  $t$ , and  $\langle \rangle$  denotes an ensemble average.

**Table 2**

Simulation parameters and some physical properties of aqueous LiCl solutions. All the energies are given in kJ/mol.

System	1	2	3	4	5
Number of H <sub>2</sub> O	252	244	232	224	208
Number of ions	4	12	24	32	48
Average box length (Å)	19.62	19.50	19.38	19.25	19.02
Salt concentration (m)	0.5	1.5	3	4	6
Experimental density (g/cm <sup>3</sup> )	1.013	1.043	1.074	1.101	1.156
Calculated density (g/cm <sup>3</sup> )	1.012	1.041	1.069	1.097	1.040
$E_{\text{tot}}$	-37.419	-50.261	-69.519	-82.274	-107.851
$E(\text{H}_2\text{O}\cdots\text{H}_2\text{O})/N_{\text{H}_2\text{O}}$	-46.295	-37.812	-28.530	-21.219	-9.873
$E(\text{Li}^+\cdots\text{H}_2\text{O})/N_{\text{Li}^+}$	-747.065	-635.616	-531.318	-500.260	-473.438
$E(\text{Cl}^-\cdots\text{H}_2\text{O})/N_{\text{Cl}^-}$	-579.860	-559.575	-380.826	-363.511	-335.840
$E(\text{Li}^+\cdots\text{Li}^+)/N_{\text{Li}^+}$	52.092	222.405	531.209	750.457	1189.953
$E(\text{Li}^+\cdots\text{Cl}^-)/N_{\text{Li}^+}$	-262.053	-714.522	-438.051	-1901.464	-2812.687
$E(\text{Cl}^-\cdots\text{Cl}^-)/N_{\text{Cl}^-}$	51.342	220.302	529.551	762.873	1187.844

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