



A comparison of classical interatomic potentials applied to highly concentrated aqueous lithium chloride solutions



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ABSTRACT

Aqueous lithium chloride solutions up to very high concentrations were investigated in classical molecular dynamics simulations. Various force fields based on the 12-6 Lennard-Jones model, parametrized for non-polarizable water solvent molecules (SPC/E, TIP4P, TIP4PEw), were inspected. Twenty-nine combinations of ion-water interaction models were examined at four different salt concentrations. Densities, static dielectric constants and self-diffusion coefficients were calculated. Results derived from the different force fields scatter over a wide range of values. Neutron and X-ray weighted structure factors were also calculated from the radial distribution functions and compared with experimental data. It was found that the agreement between calculated and experimental curves is rather poor for several investigated potential models, even though some of them have previously been applied in computer simulations.

None of the investigated models yield satisfactory results for all the tested quantities. Only two parameter sets provide acceptable predictions for the structure of highly concentrated aqueous LiCl solutions. Some approaches for adjusting potential parameters, such as those of Aragoes [Aragoes et al., J. Phys. Chem. B 118 (2014) 7680] and Pluharova [Pluharova et al., J. Phys. Chem. A 117 (2013) 11766], were tested as well; the simulations presented here underline their usefulness. These refining methods are suited to obtain more appropriate ion/water potentials.

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1. Introduction

Aqueous electrolyte solutions receive enormous attention because of their great importance in physical chemistry, geochemistry as well as in environmental and industrial fields. They are essential elements for biochemical reactions in living organisms, thus to understand and predict their properties is fundamental for biochemical research. Biological processes mostly take place at low and moderate concentrations, industrial and geochemical applications require information about the more concentrated solutions up to the solubility limit. Consequently, simple electrolyte solutions as well as complex biomolecules are in the center of the interest of multiple publications (see e.g. [1–3]).

Classical molecular dynamics simulation is nowadays one of the (perhaps the) most popular tools in the study of these systems. Several interaction models (force field, FF) have been developed in the past 30 years to describe simple aqueous solutions (see e.g. in Refs. [4–9]), they are also widely used for the study of more complex systems [10–13]. These interatomic potentials are suited for different water models, from the simplest 3-sites, rigid, non-polarizable models (such as SPC [14]) to the polarizable, four-site models (such as SWM4-NDP [15] with Drude oscillators, or BK3 [16] with a Gaussian charge distribution).

The van der Waals interactions between atoms are usually taken into account by the 12-6 Lennard-Jones (LJ) potential, which requires 2 parameters for each type of atom pairs [17]. More complex models (such as 12-6-4 LJ model [18], the Buckingham (or EXP6) interaction model [19] or the polarizable ion FF models [20,21]) with more parameters are also used to describe ionic interactions.

Various ionic models are also routinely applied in the simulations of simple aqueous solutions or biomolecular systems. There are several comprehensive studies (such as [4,22,23]) concerning the adaptability of these models, yet the ionic parameter sets are often chosen almost randomly, and/or ionic force field parameters developed for other (different) water models are combined (see e.g. [24–27]).

In a recent paper [23] thirteen of the most common (simple and computationally low cost) 12-6 LJ ionic force fields together with the widely used SPC/E water model [28] have been investigated for aqueous NaCl (from dilute to concentrated) solutions. The authors showed that most of the examined force fields are unable to describe adequately even basic properties of NaCl solutions in the entire concentration range. In another study [29] the concentration and temperature dependence of the self-diffusion of water in nine different electrolyte solutions was investigated. They found that none of the seven combinations of ionic and water models employed can reproduce the experimentally observed concentration dependence.

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It is not expected that a single model – especially a simple one, like the 12-6 LJ models – can predict all investigated physical and chemical properties well. But for each application it is important to make sure that the most proper one for that specific target has been chosen.

Aqueous LiCl solutions are among the most frequently investigated electrolyte solutions. LiCl has been considered for thermodynamic and structural studies due to its high solubility [30]. Li⁺, which is the smallest cation, plays an important role in biological, medical and technical applications (see e.g. [31,32]). Several papers using MD simulations with different force field parameters have been published (e.g. [25–27,33,34–47]). However to the best of my knowledge, there is no study which collects and compares the available ionic force fields for aqueous LiCl solutions.

In this report 12-6 LJ ionic interatomic models of LiCl solutions, developed for rigid, non-polarizable water models, are investigated. They are used for simulating highly concentrated aqueous solutions. Their predictions about some basic physical and chemical properties (density, static dielectric constant, self-diffusion coefficients) are examined and compared to experimental values. Structure factors calculated from the atomic configurations are compared to total scattering structure factors from neutron and X-ray diffraction measurements reported earlier [48]. Some combinations of force field parameters applied in recent publications are also tested.

2. Methods

2.1. Molecular force fields

Pairwise additive non-polarizable intermolecular potentials were tested, which describe the interaction energy between two atoms or ions via the Coulomb potential

$$V_C(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (1)$$

and the 12-6 LJ potential:

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] = \epsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^6 \right] \\ = \frac{C_{12,ij}}{r_{ij}^{12}} - \frac{C_{6,ij}}{r_{ij}^6} \quad (2)$$

Here r_{ij} is the distance between two particles, i and j , q_i and q_j are the point charges of the two particles and ϵ_0 is the vacuum permittivity. The 12-6 LJ potential defines the energy with two parameters: ϵ_{ij} (the well-depth of the potential) and σ_{ij} (or $R_{\min,ij}$, the size parameter).

For a proper definition of the interaction potential the ϵ_{ij} and σ_{ij} parameters should be known for every possible i and j pairs. In the studied force field parameter sets either the ion-water (ion oxygen) parameters (ϵ_{iO} and σ_{iO}) or the ion ϵ_{ii} and σ_{ii} (or $R_{\min,ii}$) and the water ϵ_{OO} , σ_{OO} are given and the unlike parameters can be calculated according to a given combination rule (in all the water models applied here $\epsilon_{HH} = 0$). The commonly used combination rules are the geometric combination rule and the Lorentz-Berthelot (LB) combination rule. For ϵ_{ij} both of these use the geometric average:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (3)$$

The σ_{ij} is equal to the geometric average in the geometric combination rule:

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \quad (4)$$

According to the Lorentz-Berthelot combination rule σ_{ij} is equal to the arithmetic average:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (5)$$

ϵ_{iO} and σ_{iO} can be calculated applying the combination rules. One should be careful to use the proper combination rule (i.e. the one, specified in the original paper of the given FF), as was shown by Åqvist in an early paper [49].

Several of the investigated models focus on the ion-water interaction only, probably because most of them were calibrated by simulations in which a single ion was placed into water, thus only ion-water and water-water interactions were present. However in solution with finite (moderate or high) concentrations the ion-ion interactions are not negligible. The proper balance between the different ion-ion potentials (anion-anion, cation-cation and anion-cation) could be critical [13, 41]. In most cases, however, the cation-anion parameters are not given separately. The users of these FFs apply one of the combination rules to calculate the cation-anion parameters. It has been recently demonstrated that this (mostly arbitrary) choice has, in some cases, a strong influence on the results of the simulation [50]. In this study I have applied the combination rule used for the calculation of the ion-water parameters to determine the cation-anion ϵ and σ values as well.

The ionic interatomic potentials will be discussed in detail in Section 3. The ϵ_{ij} , σ_{ij} and q_i values for the models are collected in Table 1 together with the respective water model and the applied combination rule. The charges of the ions are $+1e$ for Li⁺ and $-1e$ for Cl⁻ in most of the force fields (e is the electron charge). All of the calculated ϵ_{ij} and σ_{ij} parameters are given in the Supplementary material (Table S.1).

The investigated ionic interatomic potentials are developed for the simplest, and thus extensively used rigid, non-polarizable water models. These water models are: SPC/E [28], TIP4P [51] and TIP4PEw [52]. They are perhaps not the best rigid, non-polarizable water models (according to Ref. [53] the performance of the TIP4P/2005 [54] model is better than that of the SPC/E or TIP4P models); however, the ionic potential parameters were originally developed by adjusting to one of the above mentioned three water models. Since changing the water model alters the relevant ϵ_{ij} and σ_{ij} parameters, an appropriate investigation requires the application of the same water potential parameters that have been originally tested. Thus the performance of the ionic FFs with the original water models was analyzed here. (Some of the FF sets presented below were also determined in combination with the SPC [14] or TIP3P [51] water models (see Section 3), which water models perform even more poorly, thus they are not investigated here.) The SPC/E model is a 3-site model (the 3 coordinates are the position of the point-like oxygen and the two hydrogen atoms), while the others use a fourth, virtual site, which has a role in the charge distribution: the “charge of the oxygen atom” is located at the position of the virtual site. The parameters of the water models are collected in Table 2.

2.2. Simulation details

Classical molecular dynamics simulations were performed with the GROMACS software package (version 5.1.1) [55]. Simulation details were the same for all tested interatomic potentials. Usually the default settings (methods, algorithms, boundary conditions and parameters) of the GROMACS software were selected, as they are widely used in simulations.

Aqueous LiCl solutions were studied at four different concentrations; all of them were previously examined by neutron and X-ray scattering measurements [48]. Their molality values are between 3.74 and 19.55 mol/kg. The numbers of the atoms in the simulation boxes were around 10,000. The exact number of water/ion pairs and the densities at 300 K are taken from Ref. [48] and shown in Table 3. The four studied LiCl solutions will be denoted throughout

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