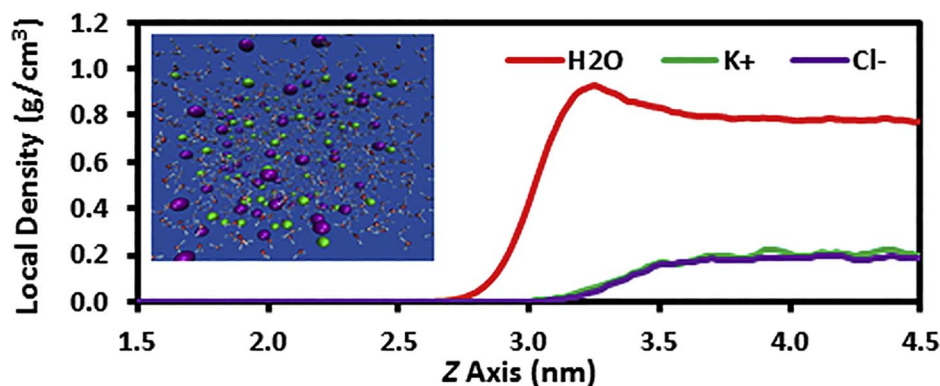# Evaluation of interfacial properties of concentrated KCl solutions by molecular dynamics simulation

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GRAPHICAL ABSTRACT

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ABSTRACT

Understanding the interfacial properties of concentrated salt solutions is critical for various applications in physical, chemical and biological processes. This study aims to evaluate the interfacial properties of potassium chloride (KCl) solutions with concentrations ranging from 1 to 4M using the molecular dynamics simulation technique. We used two different water models, TIP4P/2005 and SPC/E to calculate the local density and angle distribution, viscosity, interfacial tension and surface potential of the salt solutions. The surface tension values predicted by the TIP4P/2005 model showed an incremental trend in agreement with experimental data. For viscosity, the predictions of TIP4P/2005 are close to the experimental data, while the predictions of SPC/E are in poor agreement with the measured viscosities. Our results show that the selection of water models significantly affects the structure properties of concentrated KCl solutions. Also, the TIP4P/2005 model compares very closely with the measured interfacial properties of salt solutions.

1. Introduction

Potassium is one of the three basic plant nutrients and is a non-substitutable compound in agriculture for maintaining and expanding food production in the world. The usage in agriculture accounts for about 95% of potash produced in the world with other minor usage in the soap, plastic and pharmaceutical industries [1]. The selective froth flotation of KCl crystals from other salt crystals in their saturated brines is the main metallurgical process for recovering the potash ore along with crystallisation [2]. The flotation process of soluble salt minerals such as potash occurs in saturated solutions owing to the high solubility of these salt minerals. The presence of salt ions in the concentrated salt

solution determines the efficiency of the salt flotation as the ions influence adsorption of the required reagent to the air-water and water-salt crystal by affecting the interfacial water structure [3]. Although froth flotation of KCl has been developed and used as a conventional commercial process in the industry, the mechanism of flotation, particularly the adsorption of chemicals onto the salt is still not completely understood. Several theories have been proposed to explain the underlying mechanism of adsorption of collectors/surfactants in salt flotation [4–7] and were comprehensively reviewed by Du et al. [8]. The hydration state of ions has been shown to have a significant role in flotation of soluble salts [3,8,9]. The general effect of salt solutions is attributed to the ion-specific effect on water structure, which depends on the nature of the cation and anion species in a solution and their interactions with the solvent (water) molecules [10]. The effect of ions on the water structure depends on ion charge density and whether the water–water interactions in bulk solutions are comparable to ion-water interactions [11]. Based on these interactions ions are classified as structure-makers (kosmotropes) with high charge density that are tightly bound to the adjacent water molecules and structure-breakers (chaotropes) with low charge density that are loosely bound to the adjacent water molecules. The strong ion-water interactions in structure-making salts make the adsorption of collectors difficult, unlike structure-breaking salts where collectors adsorb on the surface of salt particles by replacing the loosely bound water molecules. Therefore, understanding the role of ions at interfaces, particularly air-brine interface is of great importance in order to enhance the efficiency of salt flotation [4,6,12].

Molecular dynamics (MD) simulation as a key tool has been used to investigate the water/water, water/ion and ion/ion interactions to estimate both equilibrium and dynamic properties of brine solutions [13,14]. Most early research focused on the thermodynamics of solvation of simple alkali or halide ions at an infinite dilution [15–19]. MD simulation has also been used to predict the surface tension of alkali halide salt solutions. So far, only qualitative agreement between the MD simulation results and the experimental data has been achieved; that is, the simulation results confirm that the surface tension of alkali halide solutions increases with increasing salt concentration. However, systematic investigations of interfacial properties of concentrated alkali halide solutions at concentrations up to their saturation point by MD simulation are still limited [3].

Furthermore, the water model used in most of the simulations is the simple point charge/extended (SPC/E) model or its polarisable model (PROL), while few reports cover other water models [16,18,20–22]. Berendsen *et al.* [23] proposed the SPC/E model by incorporating the self-energy part to account for polarization. The SPC/E water model is a three point charge model which consists of one LJ site on oxygen and three charges located at the oxygen and hydrogen atoms. Later on, Abascal et al. developed a new non-polarisable water model referred to as TIP4P/2005 which also explicitly accounts for polarisation [24]. This model has the bond geometry: the length of the OH bond is 0.9572 and the angle of H-O-H is 104.52°. This model moves the negative charge off the oxygen site and create mass-less charged sites, denoted as M site. The location and magnitude of the negative charges is the major difference between SPC/E and TIP4P/2005. This water model has been extensively examined for its prediction of thermodynamic and dynamic properties of pure water at different temperatures and pressures. This model was classified as the best model in comparison with other water models [25,26]. Also this water model has been successfully used to calculate the surface tension of water and water-alcohol mixtures [27,28]. Song and Dai [29], Gonzalez and Abascal [30] compared the predicted shear viscosity of five major water models including SPC/E and TIP4P/2005. The results indicated that the TIP4P/2005 model's prediction was the closest to the experimental data, while the SPC/E model underestimated the experimental data. However, this water model has not been used to investigate the interfacial properties of concentrated salt solutions despite all the merits of TIP4P/2005 water

model. Therefore, this paper aims to examine the TIP4P/2005 and SPC/E models to predict interfacial properties of aqueous KCl solutions at salt concentrations of 1–4M. Surface tension and surface potential are evaluated and validated against simulation results and/or experimental data if available. This study aims to provide insights on how different water models predict the interfacial properties of salt solutions.

2. Methods

2.1. Interaction energy models

The isotropic site–site potential was used in this simulation. The pair potential $U(r_{ij})$ consists of the sum of interactions between site "i" and site "j" separated by distance r_{ij}. These interactions are spherically symmetrical and depend on the distance between these sites. The equation for this potential is described as follows [31]:

$$U(r_{ij}) = 4 \sum_{i=1}^{NLJ} \sum_{j=1}^{NLJ} \varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} + \sum_{i=1}^{NCL} \sum_{j=1}^{NCL} \frac{q_i q_j}{r_{ij}} \tag{1}$$

where the first and second terms on the left hand side represent the 12-6 Lennard–Jones (LJ) dispersion and repulsion interactions. The third term describes the Coulomb law of electrostatic interaction (CL). q_i and q_j are the charges of sites. ε_{ij} and σ_{ij} are the combined LJ well-depth and collision diameter of the two sites calculated based on the Lorentz-Berthelot mixing rules [32]. NLJ and NCL are the number of LJ and CL interaction sites in the system.

For the water interaction models, the TIP4P/2005 model [24] was employed in the simulations. It consists of one LJ central site located on oxygen nucleus and three coulomb sites. The SPC/E water model included in GROMACS was also used for comparison. The OPLS model for ions described by Jorgensen [33,34] is used as they are the default in the OPLS force field distributed with the GROMACS package. The standard geometric combination rules for the OPLS model were used to obtain the LJ parameters between atoms of different species in both sets of potential parameters as shown in Table 1.

2.2. Simulation procedure

Simulations were performed at the canonical NVT ensemble (at a constant amount of substance (N), volume (V) and temperature (T)) by using the GROMACS package [35]. Temperature was fixed at 300 K by using v-rescale. Both LJ and electrostatic interactions were truncated at 1.2 nm. Long-range electrostatic interactions were corrected by the Ewald summation method using Particle Mesh Ewald for the reciprocal part [30]. The simulation box size was fixed at around 3.0 nm, which is adjusted according to the system density for bulk phase. To mimic the vapour-liquid interface, two empty boxes with the same geometry, were added on each side of bulk box of liquid along *z*-axis (as shown in Fig. 1). Each simulation was performed at a constant number of ions and water associated with different concentrations as shown in Table 2. The leapfrog method with a time step of 1fs was used to integrate the particle motion. A total simulation time of 3ns including 500ps for equilibrium period and 2500ps for sampling stage was used to calculate the properties [5].

Table 1
Potential parameters of water and ions.

Model	σ (nm)	ε (KJ/mol)	charge	dOH (nm)	H-O-H (°)	dOM (nm)
TIP4P/2005	0.3159	0.7749	−1.1128	0.09572	104.52	0.01546
SPC/E	0.3166	0.6502	−0.8476	0.1	109.47	0
K$^+$	0.4930	0.0014	1	–	–	
Cl$^-$	0.4420	0.4930	−1	–	–	