Structural and dynamical properties simulations of potassium fluoride aqueous system at various temperatures from 298.15 K to 358.15 K

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Abstract. The energy storage systems are dominated by lithium-ion based chemistry. Currently, the focus has shifted to its nearest neighbours and extensive studies have been carried out on sodium and potassium ion-based batteries. Incorporation of potassium fluoride into solar cells (CIGS) improves the conversion efficiency by increasing the majority carrier concentration. In this study, we present results from molecular dynamics simulations of water solutions and clusters containing potassium fluoride with the interatomic interactions described by OPLS-AA force field for understanding the mechanisms of the physical phenomena of these ionic complexes. The structural and dynamical properties of KF solutions have been studied at various temperatures using TIP4P water model and the ions which are modeled as charged Lennard-Jones particles. The analysis of the simulation results showed that the temperature has decisive effects on the physicochemical properties of the KF electrolyte in aqueous solutions.

Keywords: Molecular Dynamics; Self-diffusion coefficient; Dielectric constant; Potassium Fluoride; Potassium-ion batteries.

1 Introduction

Considering the fact that lithium is a scarce element, consisting of only 0.0017% by weight of earth's crust, it is most likely that we may face a lithium crisis in near future. In contrast, the potassium element is more abundant than lithium comprising 2.09% of the earth's crust by weight which makes it cheaper than lithium. This ensures adequate supply and low cost of raw materials. We can say that any battery technology based on potassium will be cheaper than lithium based systems if other electrochemical and economic factors remain same. It is in this context that potassium-ion batteries become a hot topic recently in research field. The energy density of KIBs is relatively high which arises out of the standard reduction potential of K^+/K (-2.936 V) which is close to Li^+/Li (-3.04 V) [1, 2].

In addition, the potassium fluoride system maximizes the efficiency of (CIGS) solar cells compared to the traditional values [3, 4]. The numerical simulation of

these solutions is an important method in understanding the mechanisms at the interfaces relevant to many applications and natural processes [5-8].

The present investigation is a continuation of our research works focused on the dynamics of aqueous solutions [9]. However, hydration of K^+ and F^- ions and its effects on water structure in various temperatures were studied using molecular dynamics (MD). This valuable approach is established to investigate the computed structural, energetic, and thermodynamic properties of present liquids.

The ionic radius of the potassium ion is considerably larger than those of lithium and sodium ions, and the charge density is correspondingly lower. The analysis of literature shows that there are just a few studies of molecular equilibrium simulations for the KF(aq) system.

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The content of this paper is the following. The simulation details of the MD simulations are given in section 2. The computed structural and dynamical properties, such as the hydration number, self-diffusion coefficient, and dielectric constant at various temperatures in section 3. The conclusion and final remarks are presented in section 4.

2 Simulation details

Molecular dynamics simulations (MD) were conducted to investigate potassium fluoride in aqueous solution. All simulations were performed with the GROMACS software package [10]. The interatomic interactions between water and the ions are pairwise additive, where the short-ranged repulsion-dispersion interactions are described through a conventional 12-6 Lennard-Jones potential [11] and the long-ranged electrostatic interactions are modeled with the smooth PME method [12]. NPT simulations were fixed at 1 bar with Parrinello-Rahman pressure coupling [13]. The MD calculation is executed for 8 000 000 steps using 0.1 fs for one time step (8 ns). In all simulations, we used the TIP4P model with four interactions sites on the three simple atoms, and on a fourth site along the symmetry axis between the hydrogen and oxygen atoms, which is referred to as the M site [14, 15]. Since, it has enjoyed success in reproducing many of several solution properties. The ion-ion and the ion-dipole interactions are represented by a combination of Coulombic and LJ potentials. The potential can be written in general as:

$$U_{ij}(r) = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

Where q_i is the charge of the i th atom (or ion). The Lennard-Jones parameters σ_{ij} and ϵ_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The values of the potential parameters q_i , σ_{ij} and ϵ_{ij} for water, K^+ and F^- ions are summarized in Table 1.

Table 1. Lennard-Jones and electrostatic parameters for the water and ions Force Fields [14, 16].

Element	q	$\sigma_{LJ}(\text{\AA})$	$\epsilon_{LJ}(\text{kJ/mol})$
K^+	+1	0.49346	0.00137
F^-	-1	2.73295	3.01248
O	0	3.15365	0.64852
H	+0.52	0	0
M	-1.04	0	0

The GROMACS simulations were run using OPLS-AA force-field [16] to describe the interatomic potentials of the ions and water components at various temperatures. The temperature is controlled by a Nosé-Hoover thermostat [17, 18]. The potassium and fluoride ions were added to a cubic ($40 \times 40 \times 40$) $\text{\AA}^3$ simulation box with 59 K^+ , 59 F^- , and 2047 water molecules.

3 Theoretical approach

The structural properties of aqueous solutions are determined by calculating the radial distribution functions (RDF) of different pairs and coordination numbers.

The radial distribution function [RDF or $g_{ij}(r)$] is a mathematical function defines the position of a pair of ions i and j and measures the probability of finding an ion i at the distance r_{ij} from ion j .

$$g_{ij}(r) = 4\pi r^2 \rho dr \quad (1)$$

The radial coordination numbers $n_{ij}(r)$ of different ions are obtained by integrating the radial distribution function, an estimate of the number of water molecules surrounding the M^+ ion between 0 and the distance $r_{\min}$.

$$n_{ij}(r) = 4\rho_i \int_0^{r_{\min}} r^2 g_{ij}(r) dr \quad (2)$$

Where $g_{ij}(r)$ is radial distribution function for the i - j pair, ρ_i to the minimum of the first peak in RDF function.

The most common quantity to describe the dynamical behavior of aqueous systems is its self-diffusion coefficient D .

The translational self-diffusion coefficient can be obtained from the long-time limit of the Mean Square Displacement (MSD) by the Einstein relation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \frac{1}{N} \sum_{i=1}^N \langle |r_i(t_0 + t) - r_i(t_0)|^2 \rangle \quad (3)$$

Where $r(t + t_0)$ is the position vector of the centre of mass of the molecule (or ion) at time t .

The dielectric constant of non-polarizable fluids was computed from fluctuations [19] of the total dipole moment $M = \sum_{i=1}^N \mu_i$ in the simulation volume by

$$\epsilon = \frac{4}{3k_B T \langle V \rangle} (\langle M^2 \rangle - \langle M \rangle^2) + 1 \quad (4)$$

Where k_B is the Boltzmann constant and μ_i is the individual dipole moment vector of the particle. The angled brackets denote the ensemble average.

4 Results and discussion

4.1 Thermodynamical and structural properties

The temperature is a fundamental parameter in the structural study of aqueous electrolytic systems. However, the literature has shown that the effect of temperature has not been widely developed for the KF(aq) system. First, we noticed that the calculated density of potassium fluoride solutions decreases linearly with temperature. The simulated densities, total energy and structural properties of KF(aq) solutions at various temperatures are presented in Table 2.

Table 2. Simulation values of thermodynamical and structural properties of KF(aq) at various temperatures

KF system for $m = 1.5 \text{ mol.Kg}^{-1}$	1	2	3	4
Temperature (K)	298.15	318.15	338.15	358.15
Volume (nm^3)	62.027	62.833	63.790	64.900
Density (Kg/m^3)	1.100	1.086	1.070	1.052
E_{tot} (10^5 kJ/mol)	-1.250	-1.214	-1.179	-1.143
Number Hbonds / Hydrogen	1.615	1.574	1.531	1.487
$r_{\text{min}}(\text{K-O}_w)$ ($\text{\AA}$)	2.75	2.75	2.75	2.75
Hydration number (n_{K^+})	6.21	6.09	5.96	5.84
$r_{\text{min}}(\text{F-O}_w)$ ($\text{\AA}$)	2.59	2.59	2.59	2.59
Hydration number (n_{F^-})	6.30	6.26	6.21	6.15

Fig. 1. Radial distribution functions $g_{\text{K-O}_w}(r)$ and $g_{\text{K-H}_w}(r)$ for potassium cation at different temperatures.

The hydration data for each species (ions and water molecules) are computed from canonical NVT ensemble molecular dynamics simulations. We have studied the local structure of this electrolyte by means of ion–ion, ion–water, and water–water pair correlation or the radial distribution functions. The RDFs for the case of aqueous KF electrolytes having a molality $m = 1.5 \text{ mol.Kg}^{-1}$ at various temperatures from 298.15 K to 358.15 K are illustrated in Figs. 1-3. The temperature evolution causes a decrease in the height of the first peak of RDFs (Figs. 1-3). This behaviour could be explained by the increment of kinetic energies of water molecules and ions.

Fig. 2. Radial distribution functions $g_{F-Ow}(r)$ and $g_{F-Hw}(r)$ for fluoride anion at different temperatures.

The first peak of $g_{K-Ow}(r)$ was at 0.275 nm and the second shell at around 0.485 nm respectively. The structural around the fluoride anion can be evaluated by the $g_{F-Ow}(r)$ and $g_{F-Hw}(r)$. Fig. 2 show that the $g_{F-Hw}(r)$ presented two peaks at 0.165 nm and 0.299 nm, respectively. The $g_{F-Ow}(r)$ also presented two peaks, the first peak lay between those of $g_{F-Hw}(r)$ at a distance of 0.259 nm, which indicates that water molecules in the first shell were oriented in such a way that only one hydrogen atom pointed toward the fluoride anion. The magnitude and position of the peaks radial distribution functions agree closely with the previous experimental studies and computer simulations of KF electrolyte in aqueous solutions [20-24].

The coordination numbers of K^+ and F^- ions decrease almost linearly with increasing temperature, which proves the rupture of ion-water interactions and the increase of ion-ion interactions.

Fig. 3. Radial distribution functions $g_{K-F}(r)$ at various temperatures.

The variation curves of the $g_{K-F}(r)$ show three pronounced peaks, the first sharp peak at 0.265 nm corresponds to the presence of contact ion pairs (CIP), the second peak at 0.428 nm shows the presence of a solvent shared ion pair (SIP) and the third peak located at 0.664 nm represents a solvent-separated ion pair (2SIP). The peak corresponding to SIP is more intense than that of CIP and 2SIP, also the formation of CIP is very important with increasing temperature. This phenomenon could be explained by effect of the temperature where the ion-dipole interaction is less important caused by thermal agitation for KF(aq) system at $m = 1.5 \text{ mol.Kg}^{-1}$. Generally, a good agreement is observed compared to the other molecular simulations reported by Fennell and all [25].

Fig. 4. Radial distribution functions $g_{Ow-Ow}(r)$ and $g_{Ow-Hw}(r)$ for hydrogen bond network as a function of temperature.

The noticeable effects of the increase of the temperature are a decrease of the first and second peaks maximum of Oxygen – Oxygen RDFs. In Fig 4-a we report the $g_{Ow-Ow}(r)$ of KF(aq) at various temperatures and chosen molality $m = 1.5 \text{ mol.Kg}^{-1}$. They are representative of the effects of the temperature on the structure of water. The structural analysis of the water network shows that the increase of temperature leads to a disappearance of the second peak, which indicates a strong distortion of the Oxygen–Oxygen structure in KF(aq) system caused by the evolution of the temperature. Fig 4-b showed the effect of temperature on the hydrogen bond network. According to this figure, when the temperature of the solution increases, the value of the first peak of RDFs decreases. This could be explained by thermal agitation which makes the water molecules faster and subsequently the breaking of the hydrogen bond. These observations on the effect of temperature are in agreement with those of literature [26].

4.2 Dynamical properties

The new dielectric constant and self-diffusion coefficient values obtained from the molecular simulation of KF(aq) system at various temperatures and $m = 1.5 \text{ mol.kg}^{-1}$ are listed in Table 3. As presented in Fig. 5, the values of the self-diffusion coefficients gradually increase with increasing temperature. This behaviour is more pronounced for the water molecules but less for the ions. This may be related to the strong effect of the columbic forces which are more effective on the ion species. Another interesting result is that the dielectric constant variations show that its values decrease as the temperature increases. However, our simulation results agree well with other molecular simulations and experimental studies [27, 28]. In addition, the simulated dielectric constant using TIP4P water model remains low compared to that determined experimentally for pure water.

Table 3. The simulation results for the dynamical properties of water, K^+ and F^- at various temperatures, the self diffusion coefficient expressed in units of ($10^{-9} \text{ m}^2/\text{s}$).

Temperature (K)	D_{KF}	D_w	D_{K^+}	D_{F^-}	Dielectric constant (ϵ)
298.15	2.453 ± 0.052	2.567 ± 0.060	1.493 ± 0.057	0.717 ± 0.100	41.34
318.15	3.565 ± 0.117	3.719 ± 0.121	2.141 ± 0.006	1.324 ± 0.211	40.03
338.15	4.792 ± 0.142	5.029 ± 0.198	2.372 ± 0.753	1.819 ± 0.080	40.06
358.15	6.278 ± 0.277	6.564 ± 0.300	3.406 ± 0.210	2.571 ± 0.338	37.95

Fig. 5. Self-diffusion coefficients of water molecules and ions in KF(aq) system as a function of temperature.

Fig. 6. Dielectric constant (ϵ) of KF(aq) system as a function of the simulation time at various temperatures.

5 Conclusion

We have investigated the structural and dynamical properties of potassium fluoride salt solution at various temperatures ranging from 298.15 to 358.15 K by using a TIP4P water model in combination with the OPLS-AA force-field to describe the ion-ion, ion-dipole and dipole-dipole interactions in solutions. Our approach indicated that the molecular simulations are able to give microscopic and macroscopic quantities on the aqueous electrolytes.

The force-field parameters have been validated here by comparison of our results with those available in the literature from experimental data and molecular simulations. The dielectric constant values of TIP4P determined by this force-field are relatively close than those reported for comparable simulations but fall short of the experimental value of 78.4. The hydration and dynamical properties of KF(aq) solutions are so influenced by the temperature and chemical nature of counterion. However, the effect of temperature on the dynamic properties of this system is manifested by thermal agitation which varies the kinetic energy of the water as well as the ions.

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