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Molecular dynamics simulations of Lithium Fluoride aqueous solutions: Effects of ion concentration on the structural and dynamical properties at T=300 K

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Abstract

Lithium fluoride aqueous system play an important role in a variety of chemical engineering, energy, biochemistry and environmental processes. Lithium salts are also widely used in conventional electrolytes for making lithium-ion batteries. Computer simulation of lithium in fluoride aqueous solution has an important tool in understanding the structural and dynamical characteristics of ionic complexes. In this investigation, the structural and dynamical properties of supersatured LiF systems have been studied by molecular dynamics simulations at different molalities range from 0.05 up to 2.00 mol.Kg^{-1} using extended simple point charge (SPC/E) water model and the ions which are modeled as charged Lennard-Jones particles. Molecular dynamics simulations return highly complex data. The cartesian positions of each atom of lithium chloride aqueous solution are recorded at every time step of the trajectory. Therefore, the analysis of data requires to calculate the radial distribution functions (RDFs) describing the structure of the hydration shells around the ions in solutions and the hydration number. The structural properties of the water and Li$^+$ and F$^-$ ions, such as the coordination number, interparticle distance, self-diffusion coefficient and dielectric constant are strongly depending on the molality and chemical nature of counterions.

Keywords: Molecular Dynamics; Hydration number; Self-diffusion coefficient; Dielectric constant; Lithium Fluoride.

1. Introduction

For many years, molecular dynamics (MD) simulations have been established as a powerful and valuable method to investigate the molecular structure of liquids. Although there are increasingly emerging quantum mechanical techniques for many-particle systems, a classical treatment still presents the method of choice to obtain spatial and time correlation functions for model electrolyte solutions within reasonable statistical accuracy [1, 2].

Computer simulation of lithium fluoride has an important tool in understanding the dynamics of condensed phases at the molecular level. The hydration properties of fluorinated compounds are relevant to many natural processes and industrial applications including chemistry [3, 4] environmental science [5] and energy [6, 7].

Lithium is the most attractive anode material for high-energy density rechargeable batteries. Enriching the solid electrolyte interphase (SEI) with lithium fluoride (LiF) has recently gained popularity to improve Li cyclability [8].

The lithium fluoride aqueous solution is subjected to hydrolysis, and susceptible to forming complex ion $(Li(H_2O)_n^+)$ in solution. The experimental hydration numbers of Li$^+$ ion vary between the values of 4 and 6. The hydration numbers of Li$^+$ were considered to be dependent on temperature and salt concentrations, with higher salt concentrations resulting in lower hydration numbers [9-11].

The hydration phenomenon of the LiF(aq) system depend on the various interactions ion-ion, ion-water and water-water. These interactions are influenced by the ion size and therefore the variation in charge density.

However, the coordination number strongly depends on the nature of the ions constituting the electrolyte aqueous system among other things the charge density $[ne/(\frac{4}{3}\pi r^3)]$ for each ion, where r is

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the ionic radii, e is the electron charge ($1.6 \ 10^{-19}$ C), and n represents the ion charge. Indeed, the charge density of the ions present in our system having the following order: Li^+ (98 C.mm^{-3}) > F$^-$ (24 C.mm^{-3}) [12].

The lithium is the smallest one in the series of alkali metal ions and has the highest charge density. Many structural studies of solutions of alkali metal salts are devoted to hydrated complexes of lithium ions. A large number of works have been undertaken to identify the structure forming and structure breaking properties of ions.

The outline of this paper is the following. The simulation details of the MD simulations are given in section 2. The computed structural properties, self-diffusion coefficients and dielectric constants are determined in section 3. The conclusion and final remarks are presented in section 4.

2. Simulation details

Equilibrium molecular dynamics (MD) simulations of lithium in fluoride aqueous solution have been investigated using the GROMACS package [13]. The density of the system is adjusted to reflect the composition of the specific solution being simulated. Coulombic interactions were evaluated with the smooth PME method [14]. Canonical ensemble simulations (NPT), for which the particle number N, as well as the pressure were fixed at 1 bar with Parrinello-Rahman pressure coupling and the temperature T = 300 K [15]. The MD calculation is executed for 3 000 000 steps using 0.1 fs for one time step. In all simulations, we used the simple three-site extended single point charge (SPC/E) model [16] for the water molecules because of its performance combined with a reasonable description of structure and dynamic properties, which is known to also give an appropriate description of several solution properties. The ion–ion and the ion–water interactions are represented by a combination of Coulombic and LJ potentials [17]. The potential can be written in general as:

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

Where q_i is the charge of the ith 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

$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The Lennard-Jones parameters used in this work are summarized in Table 1.

Table 1. Lennard-Jones and electrostatic parameters of ions

Element	Charge (**q**)	σ_{LJ} (Å)	ε_{LJ} (kJ/mol)
Li$^+$	+1	2.12645	0.07648
F$^-$	-1	2.73295	3.01248
O	-0.8476	3.16560	0.65017
H	+0.4238	1	0

During dynamic simulations, the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force-field [18] was employed to describe the interatomic potentials of the ions and water components. The simulations were performed at 300 K. The temperature is controlled by a Nosé-Hoover thermostat [19, 20]. The lithium and fluoride ions were added to a cubic (40 × 40 × 40) Å^3 simulation box with 2165 water molecules.

The structure of the liquid was characterized by calculating the pair distribution functions (RDFs) of different pairs and the radial coordination numbers. 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$^+$ particle between 0 and the distance r_{min}.

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

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

3. Results and discussion

3.1 Thermodynamical and structural properties

The computed densities, total energy and structural properties of aqueous LiF solutions at different concentrations are presented in Table 2. The specific density of aqueous lithium fluoride solutions is an increasing linear function of electrolyte molality. However, this count is reversed for the number of hydrogen bonds at a given temperature T = 300K.

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The hydration structural properties for each aqueous ion (Li^+ and F^-) are computed from canonical ensemble simulations (NVT), for which the particle number N, as well as the system volume V and the temperature T = 300 K. It is convenient to study the local structure of an electrolyte solution by means of ion–ion, ion–water, and water–water pair correlation or the Radial Distribution Functions (RDFs).

The RDFs for the case of saturated aqueous LiF electrolytes at various molalities from 0.05 to 2 mol.Kg^{-1} are presented in Figs. 1-4. The effect of concentration has been reported. Increasing molality for the cases of Li^+–O_w, Li^+–H_w, F^-–O_w, F^-–H_w, O_w–O_w and O_w–H_w RDFs causes to decrease in the height of the first peak.
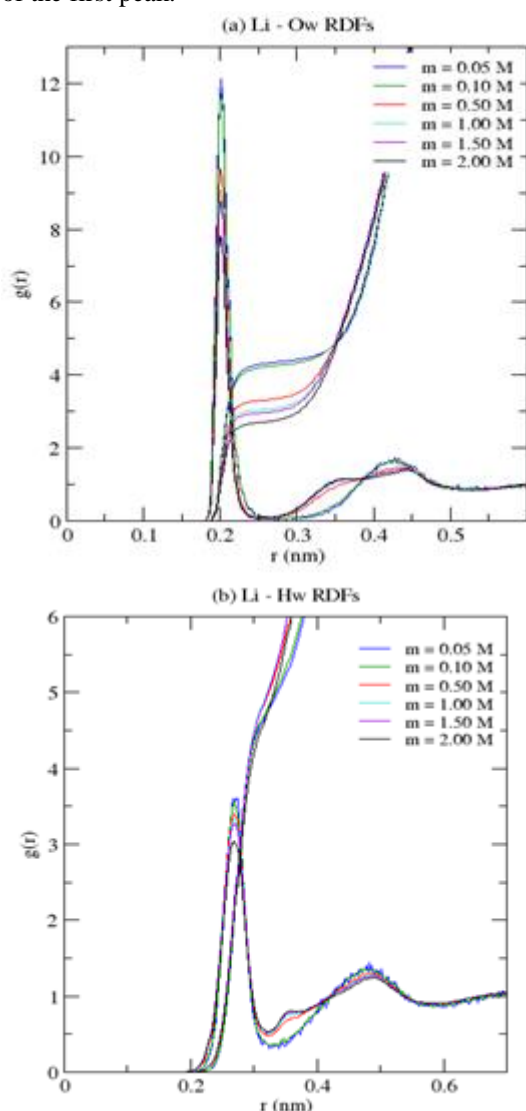

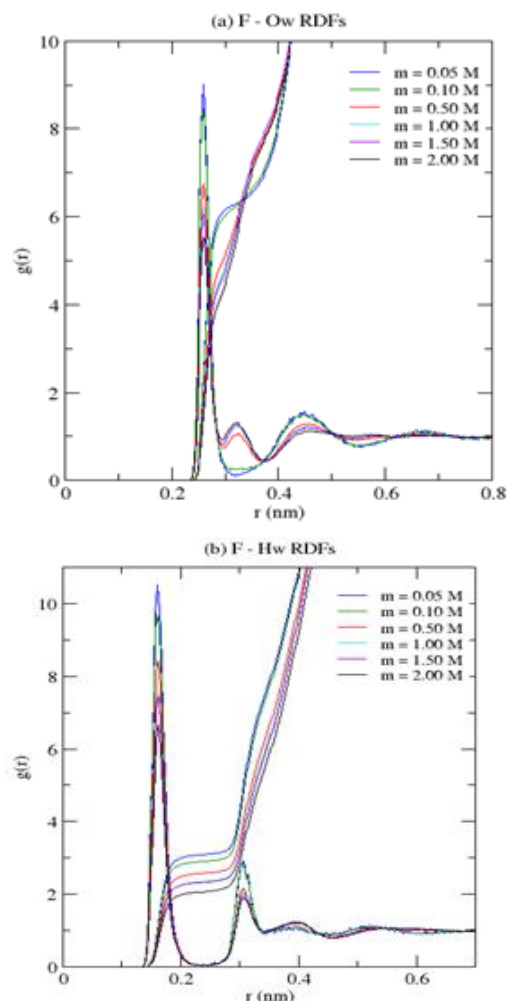Figure 1. Radial distribution functions $g_{Li-Ow}(r)$ for lithium cation at various concentrations

Figure 2. Radial distribution functions $g_{F-Ow}(r)$ for fluoride anion at different concentrations

The first peak of $g_{Li–Ow}(r)$ was at 0.203 nm and the second shell at around 0.428 nm respectively. The magnitude and position of the first peak in Li^+–O_w radial distribution functions agree closely with the previous computer simulations [21-24].

The structural around the fluoride anion can be evaluated by the $g_{F–Ow}(r)$ and $g_{F–Hw}(r)$. Figs. 2-a and 2-b show that the $g_{F–Hw}(r)$ presented two peaks at 0.161 nm and 0.307 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 0.261 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. When the salt concentration increases, new $g_{Li-Ow}(r)$ and $g_{F-Ow}(r)$ peaks will appear around 0.322 nm and 0.358 nm respectively. This behaviour could be explained by the appearance of a new phase in the supersaturated LiF electrolytic system. The coordination numbers of Li^+ and F^- ions decrease significantly with increasing

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concentration; witch proves the rupture of pairing ions and the increase of separated ones. The results of our simulations are consistent with X-ray diffraction and neutron diffraction experimental results for other electrolytic systems containing lithium and fluoride ions [25-27].

Table 2. Simulation values of thermodynamical and structural properties of LiF(aq) at various concentrations

| LiF systems at T = 300 K	1	2	3	4	5	6
Molality (mol/Kg)	0.05	0.10	0.50	1.00	1.50	2.00
Volume (nm^3)	64.72	64.52	63.25	61.82	60.37	59.29
Density (g/cm^3)	1.000	1.003	1.019	1.037	1.056	1.070
Total Energy (10^5. kJ/mol)	-0.870	-0.890	-1.053	-1.247	-1.451	-1.646
r_{min}(Li-O$_w$) (Å)	2.03	2.03	2.03	2.03	2.03	2.03
Hydration number (n_{Li+})	4.32	4.23	3.30	3.04	2.95	2.70
r_{min}(F-O$_w$) (Å)	2.61	2.61	2.61	2.61	2.61	2.61
Hydration number (n_{F-})	6.33	6.29	6.11	6.04	5.93	5.76
Number Hbonds /Hydrogen	1.794	1.788	1.755	1.718	1.677	1.651
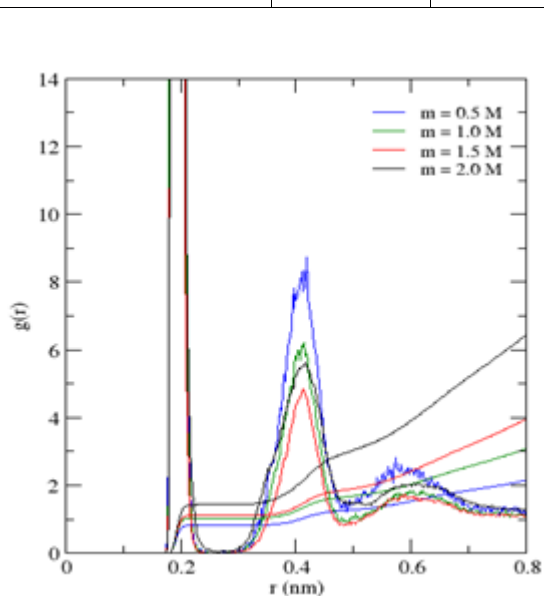
Figure 3: Radial distribution functions $g_{Li-F}(r)$ at various concentrations

The $g_{Li-F}(r)$ curve shows a pronounced two intensive peaks, the first sharp peaks at 0.195 nm correspond to the presence of Contact Ion Pairs (CIP) and the second peaks at 0.403 nm show the presence of Solvent-Shared Ion Pair (SSIP). The SSIP peaks are also higher with increasing of concentration and the number of water separated ion pairs is found to be significant for this saturated solutions. A generally good concordance is obtained by comparing these simulation results with those reported in the literature by Fennell and all [28].
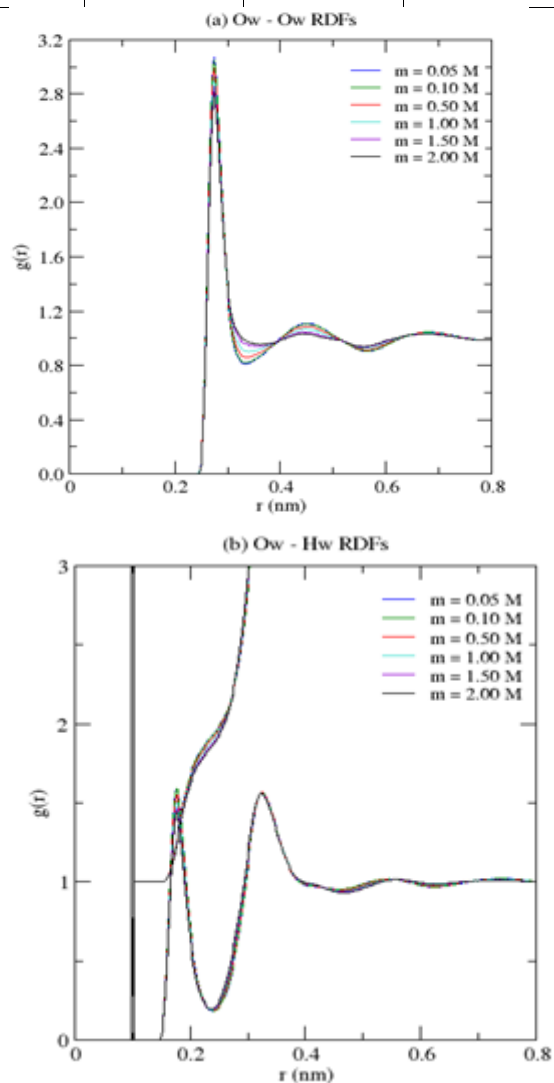

Figure 4: Radial distribution functions $g_{Ow-Ow}(r)$ and $g_{Ow-Hw}(r)$ for hydrogen bond network as a function of molality

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The noticeable effects of the increase of the concentration 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 LiF(aq) at various saturated concentrations. The position of the second peak of $g_{Ow-Ow}(r)$ moves from 3.34 – 5.68 Å to 3.64 – 5.64 Å, which indicates a strong distortion of the Oxygen–Oxygen structure in LiF(aq) system when the concentration is increased. Fig 4-b showed the effect of molality on the hydrogen bond network. According to this figure, when the molality of the solution increases, the value of the first peak of RDFs decreases. This could be explained by the strong effect of the columbic forces of ion-ion and ion-dipole which makes the breaking of the hydrogen bond. These observations on the effect of concentration are in agreement with those of other research works [29-31].

3.2 Dynamical properties

The most common quantity to describe the dynamical behavior of a aqueous system 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:

$$D = \frac{1}{6\,N} \lim_{t \to \infty} \frac{\langle \sum_{i=1}^{N}[r_i(t_0 + t) - r_i(t_0)]^2 \rangle}{t}$$
$$= \frac{1}{6} \lim_{t \to \infty} \frac{d(MSD)}{dt} \qquad (3)$$

Where r_i is the centre-of-mass coordinate vector of the i-th molecule (or ion) at time t_0 and $(t_0 + t)$ [32].

The static dielectric constant was computed from fluctuations of the total dipole moment $M = \sum_{i=1}^{N} \mu_i$ in the simulation volume by [33]

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

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

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

Molality (mol.kg^{-1})	D_{H2O}	D_{Li+}	D_{F-}	Dipole moment (D)	Dielectric constant
0.05	2.644 ± 0.001	1.188 ± 0.073	1.048 ± 0.006	2.3461	68.69
0.10	2.561 ± 0.014	1.172 ± 0.039	0.997 ± 0.062	2.3418	69.66
0.50	2.313 ± 0.094	1.129 ± 0.011	0.916 ± 0.084	2.3071	67.03
1.00	2.114 ± 0.050	0.846 ± 0.071	0.706 ± 0.069	2.2658	59.22
1.50	1.832 ± 0.095	0.591 ± 0.025	0.443 ± 0.049	2.2224	59.47
2.00	1.657 ± 0.012	0.302 ± 0.048	0.235 ± 0.009	2.1811	58.81

In Table 3 we have also reported the self-diffusion coefficients of water, Li$^+$ and F$^-$, dipole moment and dielectric constant as a function of salt concentration. The values of the self-diffusion coefficients decrease with the increase of salt concentration. This behavior can be related by the strong effect of colombic interactions between various partial charges distributed either on or near the oxygen, hydrogen atoms and ions in the saturation interval studied. Figure 5 shows that the self-diffusion coefficients of F$^-$ are lower than those of Li$^+$ and approach in the area of supersaturation.

The mobility of ions in aqueous solutions could be explained by the size of each ion. In fact, the atomic radius of lithium is greater than that of fluoride which generates several hydration layers for F$^-$ compared to Li$^+$ and consequently faster mobility of Li$^+$.
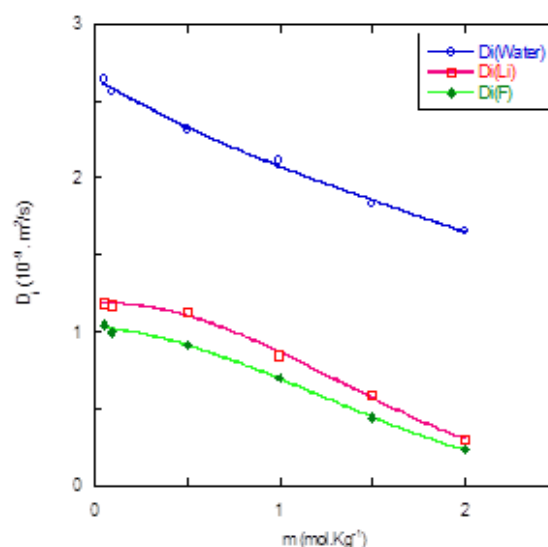

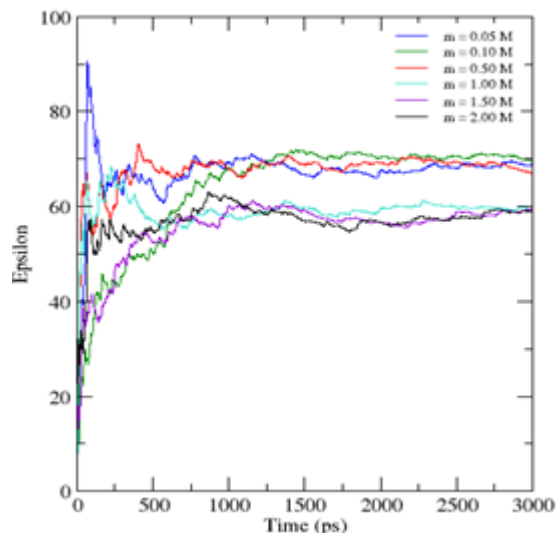**Figure 5.** Variation of self-diffusion coefficient as a function of molality

Figure 6. Dielectric constant of a LiF system as a function of the simulation time at various molalities

The dielectric constant values decreases as the concentration increases. This decrease is due to two effects. As the concentration increases, first the cations and the anions are closer to each other on average, so the average attractive interaction between them is deeper. Second, the coulomb interaction between cations and anions is less screened. the simulated dielectric constants for LiF solutions are relatively small compared to that found experimentally, this finding has been observed for other aqueous electrolytic systems which have been used the SPC/E water model [34-36].

4. Conclusion

This study examined the structural and dynamical properties of lithium fluoride solutions in saturated aqueous salts using the molecular dynamics method. The SPC/E water model was employed in combination with the OPLS-AA force-field to describe the interatomic potentials of the ions and water components. The reliability of these force-field parameters has been validated here by comparison of our results with those available in the literature from of molecular simulations and experimental techniques.

The new results obtained from this MD simulations show that the hydration structure and dynamical properties of aqueous LiF system are so influenced by the concentration and chemical nature of counterion. We found that the supersaturated LiF system induces a distortion of the oxygen-oxygen structure with a shift of the second shell and the hydrogen bond network of water is perturbed by the columbic interactions ion-ion and ion-water molecules.

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