Experimental and molecular dynamics study of the ionic conductivity in aqueous LiCl electrolytes

Are Yllo, Chao Zhang

Department of Chemistry-Ångstrom Laboratory, Uppsala University, Lägerhyddsvägen 1, 75121 Uppsala, Sweden

Abstract

Lithium chloride LiCl is widely used as a prototype system to study the strongly dissociated 1-1 electrolyte solution. Here, we combined experimental measurements and classical molecular dynamics simulations to study the ion conduction in this system. Ionic conductivities were reported at both 20°C and 50°C from experiments and compared to results from molecular dynamics simulations. In addition to provide reference data for future force fields development, the main finding in this work is that transference numbers (i.e. the fractional contribution to the ionic conductivity) of Li\(^+\) and Cl\(^-\) become comparable at high concentration. This phenomenon is independent of the force fields employed in the simulation and can be resulted from the ion-specific concentration dependence which imposes a challenge to the Debye-Onsager theory of the ionic conductivity.

Keywords: Electrolyte solution, Ionic conductivity, Molecular dynamics, Force fields, Debye-Onsager theory

1. Introduction

Aqueous electrolytes play important roles in many areas of science and engineering, such as electrophysiology, electrochemistry and colloid science. Simple 1-1 electrolyte which is completely dissociated in dilute solution is often used as a prototype system to develop analytical theories such the well-known Debye-Hückel theory \[1\]. This tradition dates back to the beginning of Physical Chemistry and coins the early physical chemists as “Ionists” \[2\].

Lithium chloride (LiCl) as an example of these simple 1-1 electrolytes is of particular interest due to its very high solubility (\(\sim\) 45 wt% at room temperature). The structure of LiCl solution has been extensively investigated by X-ray diffraction and neutron scattering experiments \[3, 4, 5\] in together with reverse Monte Carlo and molecular dynamics simulations \[6, 7, 8\]. The synergy between experiments and simulations has been proven to be useful to gain a deeper understanding of solvation structures of Li\(^+\) and Cl\(^-\).

In the molecular dynamics simulation community, another interest of modeling LiCl solution was on developing various kinds of force-fields where cations and anions are commonly described by Lennard-Jones (LJ) potential and point charge \[13\]. Despite of its simplicity, this approach has been shown be capable to capture both single ion properties (such as the hydration free energy) to ion-ion interactions as reflected in radial distribution functions and the solubility \[11\]. We refer interested readers to a recent work on this topic for a comprehensive overview and benchmarks \[12\].

On the other hand, the dynamical and transport properties of these models were often overlooked. In particular, the ionic conductivity of LiCl calculated from molecular dynamics simulations has not been compared to experimental measurements at both room temperature and elevated temperature. This fact is somehow surprising, because the basic function of any electrolyte is to serve as an ionic conductor.

In this work, we carried out both experimental measurements and molecular dynamics simulations of the ionic conductivity in LiCl solutions. Ionic conductivities were reported at both 20°C and 50°C from experiments and compared to those calculated from molecular dynamics simulations using three different force-field models \[10, 13, 14\] (See Section 2 for details) and SPC/E water \[15\]. In addition to provide reference data for future force-field developing works, the main finding of our study is that transference numbers (i.e. the fractional contribution to the ionic conductivity) of Li\(^+\) and Cl\(^-\) become comparable at high concentration. This phenomenon is independent of the force fields employed in the simulation and can be explained by taking into account the ion-pairing and ion-specific effects. The later imposes a challenge to the Debye-Onsager theory of the ionic conductivity.

2. Experimental and computational methods

2.1. Ionic conductivity measurements

The conductivity measurement of LiCl at 2, 5, 10, 15, 20, 25, 30, 35 and 40 wt% were performed with an “InLab” conductivity meter (Mettler Toledo). The conductivity meter probe used is a 4 pole InLab 738-ISM by (Mettler Toledo) which has a sensitivity range from 0.01–1000 mS/cm and gives accurate measurements up to 100°C. Before measuring, the probe was...
calibrated with a standardized 12.88 mS/cm potassium chloride (KCl) solution (Mettler Toledo). After the successful calibration of the instrument, the probe was lowered into respective solution. The measurement ran until both the conductivity and the temperature of the solution had equilibrated at a stable value. The mean of the five independent measurements were then noted as the final conductivity of that solution at 20°C.

Similar measurements were then done at an elevated temperature of approximately 50°C. The solutions were heated to 50°C by placing them in a heated water bath with an external thermometer attached to a reference plastic container with deionized water. When the solution had reached the sought-after temperature, the measurements were carried out in the same way as before.

2.2. Molecular dynamics simulations

The initial cubic box size containing simple point charge/extended (SPC/E) water molecules [13] and random distributed Li+/Cl− ions was 2.963 nm for each side. Water molecules were kept rigid using the SETTLE algorithm [16]. The Ewald summation was implemented using the Particle Mesh Ewald (PME) [17] scheme and short-range cutoffs for the van der Waals and Coulomb interaction in the direct space are 1 nm.

Three force fields (ion models) for LiCl were chosen in this study which are Joung-Cheatham III (JC-S) [13], Li-Song-Merz (LI-IOD-S) [14] and Pluharová-Mason-Jungwirth (FL) [10]. JC-S was parameterized against thermodynamic data such hydration free energy and lattice energy of salt crystal and has been validated for higher salt concentration [18, 19] at room temperature. LI-IOD-S focus on the structural aspect and was fitted to the ion oxygen distance in the first solvation shell. PL-S was tuned by scaling down the point charge of each ion by the refractive index of liquid water in order to make up the missing electronic polarization. The corresponding LJ parameters and point charges of these three models are summarized in Table [1].

In all cases, the Lorentz-Berthelot combination rule was used between two dissimilar non-bonded atoms.

Regarding the technical setting in simulations, the steepest descent algorithm was used for the energy minimization before the equilibration. The NVT (constant number of particles, constant volume and constant temperature) equilibration ran for 1 ns with the timestep of 2 ps. The temperature was then held in place using the Bussi-Donadio-Parrinello thermostat which preserves both thermodynamic and dynamic properties [20]. The follow-up NPT (constant number of particles, constant pressure and constant temperature) simulations ran for 10 ns each and trajectories were collected for conductivity calculation and structural analysis. During the NPT simulations, Parrinello-Rahman barostat [21] was employed with a reference pressure of 1.0 bar. This simulation protocol was used for LiCl solution at 2, 5, 10, 15, 20, 25, 30, 35 and 40 wt % and both 20°C and 50°C and all simulations were performed using GROMACS 4 package [22].

3. Results and discussion

3.1. Ionic conductivity and transference number

The simplest way to calculate the ionic conductivity in molecular dynamics simulations is to use the Nernst-Einstein equation [23]:

$$\sigma = \sigma_+ + \sigma_-$$

$$= \frac{q_+^2 \rho D_+}{kT} + \frac{q_-^2 \rho D_-}{kT}$$

where $\sigma$ is the ionic conductivity of the solution, $\sigma_+$ and $\sigma_-$ are ionic conductivities for cation and anion respectively, $q_+$ and $q_-$ are point charges of ions in the model, $\rho$ is the number density of the salt, $k$ is Boltzmann constant and $T$ is the temperature.

One should note that the the Nernst-Einstein equation holds only for non-interacting charged particles in a homogeneous and isotropic solvent. Thus, the ion-ion correlation is not taken into account in the formula. In other words, the ionic conductivity calculated using the Nernst-Einstein equation gives an upper bound of the actual value.

On the other hand, since $\sigma$ is a sum of individual contributions of cations and anions by construction, the transference number $t_{+/-}$ can be readily extracted as:

$$t_{+/-} = \frac{\sigma_{+/-}}{\sigma}$$

From Fig. 1a, we see that the results from JC-S is the one that comes closest to the measured and the literature values in the whole concentration range at 20°C, although three ion models seem to be equally well at lower concentrations. At 50°C (See Fig. 1b), LI-IOD-S gives results which agrees best with measured values. JC-S overestimates the conductivity for lower to
Table 1: Three ion models used in this work.

| Model       | $\sigma_{Li,Li}$ (nm) | $\epsilon_{Li,Li}$ (kJ/mol) | $\sigma_{Cl,Cl}$ (nm) | $\epsilon_{Cl,Cl}$ (kJ/mol) | $q_{Li}/q_{Cl}$ (e) |
|-------------|-----------------------|-----------------------------|-----------------------|-----------------------------|---------------------|
| JC-S [13]   | 0.1409                | 1.4089                      | 0.4830                | 0.0535                      | $+1/-1$             |
| LI-IOD-S [14]| 0.2343                | 0.0249                      | 0.3852                | 2.2240                      | $+1/-1$             |
| PL [10]     | 0.1800                | 0.0765                      | 0.4100                | 0.4928                      | $+0.75/-0.75$       |

mid-range concentrations and underestimates it for higher concentrations. At both temperatures, PL significantly overestimates the conductivity from mid to high concentrations. Similar behavior of PL has been reported for the diffusion coefficient of Li$^+$ and Cl$^-$ recently [12]. This is likely due to the fact that point charge of ions are scaled down in this model which leads to a much weaker ion-solvent interaction.

Both JC-S and LI-IOD-S manage to describe the parabola behavior of the ionic conductivity as a function of the concentration and to provide accurate estimates of the corresponding concentration at the conductivity maximum. The reason for the conductivity maximum comes from a tradeoff between the increase of number of charge transportors and the decrease of their mobility as the concentration goes up. When molar conductivities are plot instead (Fig. 2), one can see clearly that the mobility of ions reduces as a function of the concentration. Results of JC-S and LI-IOD-S have better agreements with experiments while PL shows a much higher deviation in the mid-to-high concentration range.

Fig. 3 shows that the transference numbers of Li$^+$ and Cl$^-$ of three models at both 20°C and 50°C. The chloride ions contribute a larger fraction of the electrical current (0.55 to 0.65) while lithium ions stand for a smaller fraction (0.45 to 0.35). However, this gap diminishes as the concentration increase and eventually the transference numbers become similar nearly the solubility limit.

3.2. Radial distribution function and ion-pairing

The reduced (two-particle) configurational distribution function $P(r_1, r_2)$ can be expressed as [24]:

$$
\rho(r_1, r_2) = N(N-1) \int dr_3 \int dr_4 \cdots \int dr_N P(r^N) \quad (4)
$$

which gives the joint probability distribution to find one particle at position $r_1$ and any other particle at $r_2$. Note that the factor $N(N-1)$ accounts for all possible pairs.

In an ideal gas, particles are uncorrelated. As a result, the $\rho(r_1, r_2)$ simply equals to $N(N-1)/V^2 \approx \rho^2$ where $\rho$ is the number density. This leads to the definition of the quantity $g(r_1, r_2)$ called the pair distribution function:

$$
g(r_1, r_2) = \rho(r_1, r_2)/\rho^2 \quad (5)
$$

This quantity reflects the density deviation from the (uncorrelated) ideal gas.

For isotropic fluid, this function depends upon $|r_1 - r_2| = r$, this makes $g(r)$ called a radial distribution function.

The coordination number, i.e. the number of neighbouring atoms within first minimum of the $g(r)$ from a central atom, is define as:

$$
n = 4\pi\rho \int_0^{r_{\text{min}}} x^2 g(x) dx \quad (6)
$$

The first and second peaks of $g_{Li^+-O}$ and $g_{Cl^-H}$ steadily decrease for all three ion models at 20°C with increasing LiCl.
concentration (Fig. 4 and Fig. 5). This is expected since the coordinating hydrogen/oxygen atoms of water molecules are gradually replaced by the counter-ions, see Table 2. In contrast, the radial distribution function of Li\(^+\)-Cl\(^-\) goes up with increasing concentration (Fig. 6) and so does the coordination number between Li\(^+\) and Cl\(^-\) which reflects the degree of ion-pairing.

![Figure 4: Radial distribution functions (RDFs) of Li\(^+\)-O RDF at 5, 10, 20, 30, 40 wt% of LiCl and the temperature of 20\(\degree\)C.](image)

![Figure 5: Radial distribution functions (RDFs) of Cl\(^-\)-H at 5, 10, 20, 30, 40 wt% of LiCl and the temperature of 20\(\degree\)C.](image)

We notice that the coordination number of Li\(^+\)-O and Cl\(^-\)-H in JS-C is less sensitive to the concentration, in contrast to other two ion models (Table 2). This may be due to the fact that the ion-pairing is much less significant in this model below the solubility limit as seen in Fig. 6.

Although radial distribution functions at 50\(\degree\)C have a similar concentration dependence (data not shown), coordination numbers of ion-water become smaller in most cases as shown in Table 2, which were expected, because hydration shells become less structured at elevated temperature. In contrast, all three ion models show that the cation-anion coordination number goes up with the temperature. This may be due to the fact that the dielectric constant of liquid water decreases with the temperature and the solvent screening is weaker accordingly.

![Figure 6: Radial distribution functions (RDFs) of Li\(^+\)-Cl\(^-\) at 5, 10, 20, 30, 40 wt% of LiCl and the temperature of 20\(\degree\)C.](image)

Table 2: Coordination numbers as defined in Eq. 6 at different concentrations of LiCl. The row starting with the model name shows the data at 20\(\degree\)C and the row starting with * shows the corresponding data at 50\(\degree\)C.

| wt% LiCl | 5  | 10 | 20 | 30 | 40 |
|----------|----|----|----|----|----|
| JC-S: Li\(^+\)-O | 4.19 | 4.16 | 4.10 | 3.87 | 3.19 |
| * | 4.20 | 4.17 | 4.08 | 3.83 | 3.20 |
| LI-IOD-S: Li\(^+\)-O | 3.73 | 3.30 | 2.79 | 2.34 | 2.02 |
| * | 3.63 | 3.2 | 2.67 | 2.27 | 1.96 |
| PL: Li\(^+\)-O | 3.95 | 3.88 | 3.65 | 3.28 | 2.79 |
| * | 3.92 | 3.82 | 3.58 | 3.19 | 2.71 |
| JC-S: Cl\(^-\)-H | 6.81 | 6.84 | 6.85 | 6.57 | 6.37 |
| * | 6.65 | 6.67 | 6.64 | 6.37 | 5.34 |
| LI-IOD-S: Cl\(^-\)-H | 5.88 | 5.29 | 4.50 | 3.79 | 3.30 |
| * | 5.65 | 5.06 | 4.18 | 3.63 | 3.12 |
| PL: Cl\(^-\)-H | 5.56 | 5.50 | 5.11 | 4.65 | 3.91 |
| * | 5.29 | 5.27 | 4.90 | 4.32 | 3.64 |
| JC-S: Li\(^+\)-Cl\(^-\) | 0.00 | 0.01 | 0.03 | 0.18 | 0.82 |
| * | 0.01 | 0.02 | 0.07 | 0.24 | 0.81 |
| LI-IOD-S: Li\(^+\)-Cl\(^-\) | 0.62 | 0.96 | 1.35 | 1.75 | 2.03 |
| * | 0.67 | 1.01 | 1.46 | 1.81 | 2.09 |
| PL: Li\(^+\)-Cl\(^-\) | 0.05 | 0.12 | 0.35 | 0.71 | 1.19 |
| * | 0.07 | 0.16 | 0.4 | 0.78 | 1.26 |
3.3. Ion-pairing contribution to the ionic conductivity

We mentioned at the beginning of Section 3.1 that the ionic conductivity calculated from the Nernst-Einstein equation provides an upper bound and the actual conductivity is always smaller because of the ion-pairing. Near the solubility limit, the ionic conductivity may be reduced by 30% when ion-ion correlations are taken into consideration in the calculation [25]. This is similar to our estimation based on the mean square charge displacement [1][26], which gives a value of 40% for LiCl. Therefore, the overshooting of PL in the ionic conductivity at high concentration as shown in Fig. 1 is not because of the missing of ion-pairing contribution in Eq. [2] but likely due to the down-scaling of the charge in the model (See Table[1]).

One of the main observations in this study is that the transference number of the chloride ion becomes similar to that of the lithium ion. This is in accord to the tracer diffusion measurement reported in the literature [27]. The standard explanation for this phenomenon is that lithium and chloride ions pair up at high concentration and move together in a concerted manner.

Instead, we notice that the relative reduction of the Cl\(^-\) conductivity with the increase of the concentration can be notably larger than that of the Li\(^+\) conductivity and this difference becomes more apparent at higher temperature, as shown in Fig. 7. This suggests that the concentration dependence of the molar conductivity can be ion-specific. Since the molar conductivity of the chloride ion at infinite dilution is larger than that of the lithium ion, therefore this ion-specific concentration dependence will lead to a crossover between cation transference numbers and anion transference number even without considering the ion-pairing.

According to the Debye-Onsager theory for the ionic conductivity, such concentration dependence is due to a combination of electrophoretic effect and time-of-relaxation effect [1]. Overall, the electrical forces on each ion is reduced and the mobility becomes smaller. Nevertheless, the standard theory would suggest the same concentration dependence for both Li\(^+\) and Cl\(^-\). In this regard, what is shown in Fig. 7 imposes a challenge to the standard theory of the ionic conductivity and should be explored further.

4. Conclusion

In this work, we carried out both experimental measurements and molecular dynamics simulations of the ionic conductivity in LiCl solutions. Ionic conductivities were reported at both 20\(\degree\)C and 50\(\degree\)C from experiments and compared to those calculated from molecular dynamics simulations using three different ion models. In addition to provide reference data for future force-field developments, the main finding of our study is that transference numbers of Li\(^+\) and Cl\(^-\) become similar at high concentration. This phenomenon is independent of the force fields employed in the simulation and may impose a challenge to the standard theory of the ionic conductivity because of the ion-specific concentration dependence found here.

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