The dielectric properties of LiOH aqueous solution under external electromagnetic fields by Molecular Dynamics Simulation

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Abstract

Molecular dynamics simulation of LiOH aqueous solution has been performed both in the absence and presence of the external electromagnetic (E/M) fields (2.45 GHz). The simulated dielectric constant results from the fluctuation method (69.3) and electric field method (70.12) are in quantitative agreement with experiments result (64.5). The radial distribution function and coordination structure of Li⁺ and OH⁻ ions of LiOH aqueous solution change significantly with the intensity of the external E/M fields in the range of 0 and 3×10⁹ v/m. At the high E/M fields (3×10⁹ v/m), the interactions of the Li⁺ and OH⁻ ions with water in first hydration shell is weakening due to the acceleration rotational effect of ions driven by the external E/M fields. The rearrangement and interactions of water molecules around Li⁺ and OH⁻ ions in hydration shell may be affected by the external E/M fields applied.

Keywords: Electromagnetic fields; Dielectric constant; Coordination structure; Potential Mean Force

1. Introduction

Electrolyte is a very important material for natural living system and industrial processes. In particular lithium ion, one of most simple metal ions plays wide spread and diverse roles in biological, medical, and technical application [1-4]. As a

consequence, it has been frequently chosen as subjects of experimental and theoretical investigations. Ansell S. et al described the hydration structure of Li^+ ions in concentrated aqueous solutions by using X-ray and neutron scattering [5]. Bouazizi et al. reported the structural investigations of high concentrated Li^+ aqueous solution by X-ray scattering and MD simulations approach [6, 7]. The hydration structures and dynamics of Li^+ and OH^- ions in aqueous infinite dilute solutions at sub and supercritical water conditions are investigated by molecular dynamics simulations [8]. However, the water structures and the dynamics of Li^+ ions aqueous solution under the microwave radiation conditions are seldom reported. Hence, we consider and discuss the microscopic dynamics information of Li^+ ions aqueous solution under external E/M fields. It is a basic and important work for the interpretation of the microwave radiation on the electrode materials for Li-ion batteries and industrial applications of microwave processing.

Here, we choose a modified version of the GROMACS 4.5.5 [9] simulation package with the SPC/E [10] model and the OPLS-AA potential characterizing the water, respectively. This model can provide a reasonably good prediction of the structure and dielectric constant of water at the conditions of interest [11]. The simulation details and results are described and discussed in Section 2 and Section 3, respectively. In this paper, we calculate the dielectric constants of LiOH aqueous solutions using the fluctuation method and external field method, and compared with experimental data for investigating the accuracy of force fields used in this study. The water structural changes and dynamics of LiOH aqueous solution with 0.2 M and 2 M concentrations are calculated and discussed under external E/M fields. Further, the behaviors of Li^+ -OW (The O of water is defined OW) and OH^- - H_2O interactions are explained energetically using a PMF (Potentials of Mean Force) calculation in the absence and presence of the external E/M fields.

2. Computational method and Simulation details

The simulations were performed using a modified version of the GROMACS 4.5.5 [9] simulation package with the SPC/E [10] model and the OPLS-AA potential

characterizing the water and LiOH molecules, respectively. Table 1 shows that the interaction parameters of the employed models. The simulations involved 2700 water molecules placed in a cubic simulation periodic box and two concentrations, i.e. 0.2 M and 2 M (molality), corresponding to 10 Li^+ , 10 OH^- and 105 Li^+ , 105 OH^- , respectively. SPC/E water molecules were added to the system from a relaxed liquid configuration at 298 K and 1 bar.

As it is prior to system relaxation MD, energy minimization was carried out with a composite protocol of steepest descent, conjugate gradient, and truncated Newton steps, using termination gradients of 5000, 1000, and 100 kJ /mol · nm, respectively. The Nose'-Hoover thermostat [12, 13] was used to maintain the equilibrium temperature at 298 K and periodic boundary conditions were imposed in all three dimensions. The trajectories of the atoms during the equilibration process were calculated using the Verlet velocity algorithm. To make sure the pressure of two systems is the same at 1 bar, the NPT ensemble was carried out in the pre-equilibrium process. And the root-mean-square (RMS) electric fields intensities were $E_{\text{RMS}}=3\times 10^5$, 3×10^6 , 3×10^7 , 3×10^8 and 3×10^9 v/m ($E_{\text{max}}=2^{1/2}E_{\text{RMS}}$) and the frequency was set to 2.45 GHz. The E/M fields were applied in the NVT ensemble to isolate the field effects from the thermal effects, and hence the simulations were effectively non-equilibrium NVT (NNVT) simulations. Note that the frequency and intensity of the E/M fields are deliberately assigned high values so that the effects of E/M fields on LiOH aqueous solutions can be readily determined within a short simulation time.

The Particle Mesh-Ewald method [14, 15] was used to compute long-range electrostatics to within a relative tolerance of 1×10^{-6} . A cut-off distance of 8 Å was applied to real-space Ewald interactions. The same value was used for van der Waals interactions. The LINCS algorithm [16] was applied to constrain bond lengths of hydrogen atoms. A leap-frog algorithm [17] was used with a time step of 1 fs. The potentials of mean force (PMF) for Li^+ and OH^- ions in aqueous solution were computed using umbrella sampling to quantify the relative strengths of Li^+ -water and OH^- -water interactions. Simulations for the PMF calculation were equilibrated for 100 ps each, and then 100 ps were used for data collection in each window. The

umbrella sampling was performed using harmonic restraints to obtain overlapping distributions of the distance between Li^+ and OH^- ions or water from approximately 9 Å apart to approximately 2 Å apart in 0.2 Å increments. The harmonic biasing potential was 240 kcal/mol in the range 1.8-4.8 Å, 120 to 240 kcal/mol in the range 5-9 Å, respectively.

Table 1

Interaction parameters of the employed models

	Atom	ϵ (kJ/mol)	σ (nm)	q(e)
SPC/E [10]	H	0	0	0.4238
	O	0.6507	3.166	-0.8476
Dang.L.X.[18]	Li	0.69	1.506	1.0
Wiener et al. [19]	O	0.6320	3.233	-1.3
	H	0.2310	2.083	0.3

3. Results and Discussion

3.1 Dielectric constant calculation and compare with experimental data

The molecular dynamics simulation (MD) method has advantage to reveal the solvation dynamics of aqueous electrolyte solution on the picoseconds time scale, but the accuracy of different force fields and water models have been controversial topics. Recently, the dielectric spectra of different electrolytes were simulated and compared favorably with experimental data. The simulated results [20, 21] show more pronounced deviations from a single-Debye form and can be well described by a Cole-Cole fit, in quantitative agreement with experiments result. We obtained dielectric constant from fluctuation and external field methods and compared with experimental data available in the literature [22].

In the fluctuation method, the variation in total dipole moment is used to calculate the static dielectric constant and equilibrium MD simulation of 1 ns or longer is used. The static dielectric constant can be calculated from the fluctuations in the total dipole moment as [23]

$$121 \quad \frac{4\pi}{3Vk_B T \epsilon_a} (\langle M^2 \rangle - \langle M \rangle^2) = \frac{(\epsilon_s - 1)(2\epsilon_{RF} + 1)}{2\epsilon_{RF} + \epsilon_s} \quad (2)$$

122 Where V is the volume, k_B is Boltzmann's constant and T is the temperature, ϵ_a is
 123 the vacuum permittivity, ϵ_0 is the static dielectric constant, ϵ_{RF} is dielectric constant
 124 of the continuum. In our simulations, we used the dielectric constant of continuum
 125 ϵ_{RF} obtained from the static dielectric constant of LiOH aqueous solutions obtained
 126 from experiments data [22]. Note that the dielectric constant of continuum
 127 ($\epsilon_{RF} = 64.5$) was set to the same value in both fluctuation and external field method
 128 simulations and calculations.

129
 130 **Fig.1.** Variation of the average dipole moment $\langle M_z \rangle$ as a function of the field strength

131 For electric field method, the average dipole moment along the direction of
 132 applied field, $\langle M_z \rangle$, linearly increases with small field strengths and deviates from this
 133 linear relationship for large field strengths, as shown in Figure 1. Static dielectric
 134 constant determination using the external field method requires the data from the
 135 linear response region of $\langle M_z \rangle$ [24]. The dielectric constant can be obtained from the
 136 external field method using the polarisation response of the system, the average dipole
 137 moment along the direction of applied field per unit volume. This can then be related
 138 to the dielectric constant [25]

$$\frac{4\pi\langle M_z \rangle}{\varepsilon_a V E_{RMS}} = \frac{(\varepsilon_0 - 1)(2\varepsilon_{RF} + 1)}{(2\varepsilon_{RF} + \varepsilon_0)} \quad (3)$$

Where $\langle M_z \rangle$ is the average dipole moment of the system along the direction of the applied field E_{RMS} . V is the volume of the system, ε_a is the permittivity of vacuum, ε_s is the static dielectric constant and ε_{RF} is the dielectric constant of the continuum. The ratio $\langle M_z \rangle / E_{RMS}$ is obtained from the slope of the linear region of variation of $\langle M_z \rangle$ with the applied external field strength.

The dielectric constants $\varepsilon(\omega)$ of systems are frequently analyzed and presented by dielectric spectra models (Cole–Cole, Cole–Davidson, Havriliak–Negami). The Havriliak–Negami model is given:

$$\varepsilon(\omega) = \varepsilon' + j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (j\omega\tau)^\alpha]^\beta} \quad (4)$$

Where $\varepsilon(\omega)$ is the complex dielectric permittivity with static permittivity ε_s and high-frequency permittivity ε_∞ , relaxation amplitude $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, relaxation times τ , α ($0 < \alpha \leq 1$) and β ($0 < \beta \leq 1$) are shape parameters for the Cole–Cole and Cole–Davidson models. It is referred to be as a measure of symmetrical broadening of the dielectric loss relaxation peak ($\alpha = 0.986, \beta = 1$) [22]. The minimum error was obtained using the Cole–Cole model Eq. (4); the experimental data and fitting data are shown in Fig.2 (b).

Fig. 2. (a) The dielectric constant of LiOH aqueous solution calculated using OPLS-AA force field. The X-axis is the simulation time (ns), the Y-axis is the value of time-dependent dielectric constant. (b) The real (blue square) and imaginary (open blue square) parts of the experimental dielectric spectroscopy [22]. The X-axis is the frequency (GHz), the Y-axis is the value of the frequency-dependent dielectric constant.

The obtained dielectric constants and calculated values of LiOH aqueous solution using OPLS-AA force field with fluctuation method and electric field method are shown in Fig. 2(a). The experimental spectroscopy and the dielectric constant fitted by the Cole–Cole model are shown in Fig. 2(b). In our simulations the obtained dielectric constants ($\epsilon_s=69.3$ and $\epsilon_s=70.12$) of LiOH aqueous solution calculated from the fluctuation method and external field method have the minimum error comparing to the fitted value ($\epsilon_s=64.5$ [22]) using dielectric relaxation spectroscopy. Our results provide a reasonably check on the accuracy of the force field (OPLS-AA) and water models (SPC/E) we are using for molecular dynamics simulation, especially OPLS-AA force field are broadly applied to investigate the water structure and dielectric constant for aqueous electrolyte solution.

3.2 Radial distribution function

To detect ions-water structural changes of LiOH aqueous solution under the E/M fields, we analyzed the radial distribution functions (RDF) in LiOH aqueous solution. There are four site-site RDFs for LiOH aqueous solution with two concentrations of 0.2 M and 2M both with and without an E/M fields. Here, we only focus on a smaller

subset of RDF as this paper analyzed.

Fig.3. Radial distribution function, g_{Li-OW} of Li^+ in aqueous solution at 298K with and without an E/M fields

The figure 3(a) and (b) presents the RDFs of the Li^+ -OW in LiOH aqueous solution with two concentrations of 0.2 M and 2M both with and without the external E/M fields. The RDFs involving the Li^+ ion show sharp first maxima in the figure 3. All the peaks drop to zero after their maximum. Altogether this shows the preferred coordination of Li^+ ion to the oxygen site of the water molecule. The first peak of the Li^+ -OW RDF at 0.198 nm has its maximum (seen in figure 3), a good match with the recent theoretical results [5-8]. The results in the current study also agree with the neutron diffraction experiments results [26-28] for different concentration of Li^+ aqueous solution, with the first maximum at the range of 0.195 and 2.07 nm. We notice that the first peak position for Li^+ in aqueous solution at infinite dilution shift slightly. When the existence of the external E/M fields in LiOH aqueous solution, it can be seen that the Li^+ -OW RDFs do not exhibit any change in the position of the first peak maxima. However, we notice that the intensities of the Li^+ -OW RDFs have a distinct change when the concentrations changes and the E/M fields strength reaches to 3×10^9 v/m, especially the second and beyond hydration shell changes of the

Li⁺-OW RDFs. This result indicates that the coordination structure of the hydration shell of Li⁺ ion changes significantly as the concentrations of the solution changes and the applied E/M fields strength increases, noting that there is an important effect of the applied high E/M fields in the coordination structure of the lithium ion in aqueous solutions.

Fig.4. Radial distribution function, g_{OH-HW} of OH^- ion in aqueous solution at 298K and under E/M fields

The figure 4(a) and (b) presents the RDFs of the OH^- -HW of LiOH aqueous solution with two concentrations of 0.2 M and 2 M both with and without the E/M fields. The RDFs involving the OH^- ion have well defined first maxima as well in figure 4. The first peak of the OH^- -HW RDFs has its maximum at 0.167 nm. Compare the recent neutron diffraction experiment and molecular dynamics simulations results presented [29] for OH -HW of concentrated NaOH solutions, the first peak of OH^- -HW RDFs (g_{O-HW} and g_{H-HW}) have a shift from 0.18 to 0.19 nm and 0.14 to 0.17 nm, respectively. Noting that hydrogen site (OH^- ion) coordinates a water molecule through a weak bond, while the oxygen site forms strong hydrogen bonds with a number of molecules. It is found that the interaction of the OH^- ion bonded water molecules network is in a manner similar to the effect of hydrogen site (OH^- ion)

coordinating water molecule.

From the figures 3 and 4, a more obvious variation of the first and beyond peak of Li^+ -OW is observed than OH^- -HW when the external E/M field strength reaches to $3 \times 10^9 \text{ v/m}$. In the figure 4 (a) and (b), we noticed that before the E/M field strength reaches to $3 \times 10^9 \text{ v/m}$, a sharp and tall peak in the OH^- -HW corresponds to the first hydration shell, followed by almost disappeared shorter and broader second peak. When the applied external E/M field strength reaches to $3 \times 10^9 \text{ v/m}$, this second peak suddenly appears a shorter and broader second peak. The emergence of the second peak is related to the H-bonding nature loss in the structure as the E/M fields strength reaches to the maximum. This result reveals that the kinetics of the hydrogen bond is accelerated as the E/M fields strength reaches to $3 \times 10^9 \text{ v/m}$. Due to the dipole energy $E_0 p_0 \approx 4.8 \times 10^{-3} \text{ ev}$ (p_0 is the electric dipole of our model water) is less than the hydrogen-bond energy of 2.5 ev per bond, leading to the sharp change of the peak when the intensity of the external E/M fields is up to $3 \times 10^9 \text{ v/m}$ (as shown in figure 5), which implies the randomization of the position and orientation of water molecules around OH^- ion in the first hydration shell.

Fig.5. The first peak of $g_{\text{OH-HW}}$ of OH^- ion in aqueous solution at 298K and under E/M fields

3.3 Coordination number

The radial distribution function (RDF) of ion-oxygen g_{i-o} was employed to calculate the average number of water molecules that were in the primary shell of the ion–water structure, n (see Eq. (5)) [30]

$$n = (N/V) * 4\pi * \int_0^{r_i} g_{i-o}(r) \cdot r^2 dr \quad (5)$$

Where N is the number of particles in the cell and V is the total volume of the cell, (r) is the radius of the first hydration sphere which corresponds to the first minimum in $g_{i-o}(r)$. The integral is evaluated over the distance of solvent molecules to the ion.

Fig. 6. The radial distribution functions of ions and the coordination numbers.

Fig.7. Snapshots of the coordination numbers of the first solvation shell: left Li^+ –water right OH^- –water

The RDFs and running coordination numbers of Li^+ -OW and OH^- -HW are

251 plotted in the figure 6. From the figure 3 and 4, it can be seen that the Li^+ -OW and
 252 OH^- -HW RDFs do not exhibit any change in the position of the peak maxima. The
 253 first minima of the RDFs of Li^+ -OW and OH^- -HW are found at 0.252 and 0.226 nm,
 254 respectively. Hence, we can obtain the first coordination numbers when running
 255 integration from zero to the first minima. The snapshots of the coordination numbers
 256 of the first solvation shell of Li^+ -OW and OH^- -HW are shown in the figure 7. For the
 257 Li^+ ion, the first coordination number is 3.986, indicating 4 water molecules within
 258 the first shell. In the solvation shell of the OH^- ion, the RDFs have the first minimum
 259 at 0.226 nm and the value of the running integration number until this point is 2.685,
 260 indicating two more water molecules within the first hydration shell. When the
 261 concentration of LiOH aqueous solution is increased to 2 M, the first coordination
 262 numbers are 3.292 and 1.553, respectively. According the recent molecular dynamic
 263 studies [5-8, 29, 31, 32], the first hydration shell of Li^+ attracts four or five more
 264 water molecules at infinite dilution. The OH^- ion can be an H-bond donor attracting
 265 one or two more water molecules in the first hydration shell, which give a good
 266 qualitative agreement with our molecular dynamics simulation study results.

267
 268 **Fig.8.** The running coordination numbers of Li^+ ion as a function of distance $r(\text{nm})$ for O atom
 269 of water and OH^- ion as a function of distance $r(\text{nm})$ for H atom of water under E/M

fields

Figure 8 shows the running coordination numbers of Li^+ -OW and OH^- -HW under external E/M fields. The running coordination numbers of Li^+ -OW and OH^- -HW are found to change very slightly before the E/M fields strength reaches to 3×10^9 v/m. From the figures 3 and 4, we also can see the coordination structure and hydration shell formation of Li^+ and OH^- ions have a distinct change when the external E/M field strength reaches to 3×10^9 v/m. These behaviors indicate that when the E/M fields strength reaches to the maximum, the position and orientation of water molecules around Li^+ and OH^- ions may be rearranged, which contributed to the dielectric constant of LiOH aqueous solution system.

3.4 Potentials of Mean Force

The behavior of Li^+ -OW and OH^- -H₂O water interactions at the concentrations of 0.2 M and 2 M can be explained energetically with a PMF calculation in which the Helmholtz free energy required to move a water molecule toward Li^+ or OH^- ions is obtained as a function of distance from Li^+ -OW and OH^- -H₂O.

Fig.9. The potential of mean force (free energy) as a function of distance from the Li^+ ion for Li^+ -OW and OH^- -H₂O water interactions in a solution at the concentrations of 0.2 M and 2 M

In the figure 9 (a) and (b), the obtained results with a PMF calculation for Li^+ and OH^- ions at the concentrations of 0.2 M and 2 M are shown. It can be found that both correlations exhibit a similar intensity change of the free energy (PMF)

corresponds to the hydration shell at the concentrations of 0.2 M and 2 M. The change in the free energy between water in the second hydration shell of Li^+ ($r > 0.34$ nm) is 1.3 kcal/mol lower in energy than water in the first hydration shell (1.5 kcal/mol) and beyond, whereas water in the first hydration shell ($r > 0.26$ nm) of OH^- ion is 0.25 kcal/mol lower in energy than water in the second shell and beyond. This suggests that over long time scales, at equilibrium, OH^- ion will prefer a complete first hydration shell of water to form a water network according to the Boltzmann distribution. There may be a part water molecule to pass between the first and second hydration shells of Li^+ ion. Thus, it is reasonable to conclude that part of the second hydration shell of Li^+ is also frozen on the DRS time scale. This conclusion is consistent with the most recent studies [33-36], which shows that it was necessary to assume the presence of four or five water molecules in both the first and second hydration shells of Li^+ aqueous solution.

Fig.10. The potential of mean force (free energy) as a function of distance from the Li^+ ion for Li^+ -OW and OH^- - H_2O water interactions in a solution under E/M fields

The PMF calculation results for Li^+ and OH^- ions under E/M fields at 0.2 M are shown in figure 10. It is noticeable that a distinct drop of the free energy (PMF) for Li^+ and OH^- ions with water outside the first hydration shell when the E/M fields strength reaches to 3×10^9 v/m, which indicates that the interactions of the Li^+ and OH^- ions with water in first hydration shell is weakening due to the acceleration

rotational effect of ions driven by the high E/M fields applied. The result appears to be in good standing with Wang et al. [37] reported the electric fields induces the rearrangement of water molecules, weakening the interactions between water molecules. As a result, the rearrangement and interactions of water molecules around Li^+ and OH^- ions in hydration shell of LiOH aqueous solution may be affected by the microwave fields applied.

4. Conclusions

In this paper, the dielectric properties of LiOH aqueous solutions are obtained from fluctuation and external field method. The dynamic and structure properties of LiOH aqueous solutions such as RDFs, coordination number, PMF (potential of mean force) are studied under E/M fields. A pronounced effect on the height of the first and second peaks for site–site pair correlation functions is observed when the external E/M field strength reaches to the maximum. The behaviors of Li^+ -OW and OH^- - H_2O water interactions under E/M fields are explained energetically with a PMF calculation. The main conclusions are as follows:

1. Due to hydration effect of Li^+ and OH^- , water molecules are bound around ions. As the concentrations of the solution changes and applying external E/M field strength increases, the coordination structure of the hydration shell of Li^+ and OH^- ions changes significantly. The kinetics of the hydrogen bond OH^- ion is accelerated as the E/M fields strength reaches to 3×10^9 V/m.
2. We explained energetically the behavior of Li^+ -OW and OH^- - H_2O interactions energies to reveal the structure changes of the hydration shell of Li^+ and OH^- ions with and without the external E/M fields using a PMF calculation. According to the Boltzmann distribution, OH^- ion will prefer a complete first hydration shell of water to form a water network. There may be a part water molecule to pass between the first and second hydration shells of Li^+ ion.
3. At high E/M fields, the interactions of the Li^+ and OH^- ions with water in first hydration shell is weakening due to the acceleration rotational effect of ions driven by

the external E/M fields. The rearrangement and interactions of water molecules around Li^+ and OH^- ions in the hydration shell of LiOH aqueous solution may be effected by the external E/M fields applied.

The dielectric behaviors of electrode materials for Li-ion batteries exposed to extreme conditions (such as electromagnetic radiation) are an interest topic. Further work will focus on the microscopic dynamics information of (such as LiFePO_4 and LiCoPO_4) at different frequencies in the absence and presence of external E/M fields by MD study.

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