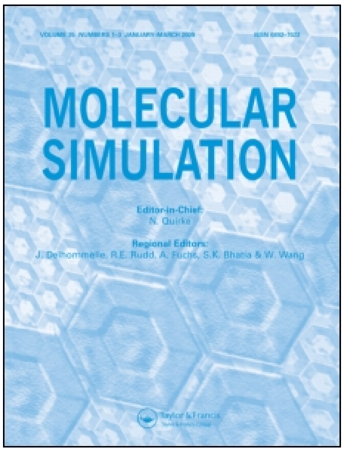

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Molecular dynamics simulation of inorganic ions in PEO aqueous solution

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Solid polymer electrolytes (SPEs), especially the ones dissolving lithium ions in poly ethylene oxide (PEO) polymer by the bonds between ether oxygen and cations, have long been investigated with the goals of developing batteries with high energy density. It has been accepted that most ions move through the amorphous polymer phase and their mobility depends crucially on the solution environment, though the detailed transport mechanism is not fully developed. Recently, ternary mixtures composed of PEO/salts in aqueous solution have been shown to display more attractive properties than binary SPE mixtures. Numerous experiments have found a dramatically changed environment for the cations and increased ionic conductivity of polymer/salts electrolytes for increased relative humidity, suggesting that the coupling between polymer chains and cations may be weakened due to the existence of water molecules. In this paper we report molecular dynamics (MD) simulation, using an optimized force field that includes polarizabilities via the dynamic shell model, to study the structural properties of inorganic ions in PEO aqueous solution and the competitive solvation of ions between water and polymer oxygen. Our simulation results show that ions are solvated more favorably by water than by polymer. This conclusion is in a good agreement with neutron diffraction by isotropic substitution (NDIS) experiments.

Keywords: Li; PEO; Water; Simulations; Polarizability

1. Introduction

One of the advanced candidates for the development of high energy density batteries are polymer electrolytes composed of inorganic salts dissolved in the polymer matrix, also known as solid polymer electrolytes (SPE) [1–3]. Their promising aspects, such as easiness to shape, environmental safety and flexible operation, permit them to replace traditional batteries being used in automotive, aerospace and portable electronics applications [1–3]. Many choices of salts are available, but lithium doped polymer electrolytes, mostly in the format of PEO/LiI, PEO/$LiCF_3SO_3$, PEO/$LiClO_4$, etc, are expected to create relatively high energy density owing to the light mass of lithium. With its capability of forming very stable lithium–polymer complexes by the interaction of its oxygen and cations, poly ethylene oxide (PEO), composed of repeated ether units ($(-CH_2-O-CH_2)_n -$), has the greatest technological and scientific interest [1].

The industrial importance of the SPEs has generated the need for fundamental research which would provide the theoretical basis for the design of new batteries with improved performance. By means of experiments and computer simulations, it has been shown that most ions diffuse through the amorphous regions of polymer and the transport mechanism are strongly controlled by the ion–ion and ion–polymer interactions [3–5]. Normally amorphous and crystalline phases coexist in the PEO and most PEO/Salts mixtures. However, when operated at room temperature, at which PEO displays a large degree of crystallinity (a barrier to ions transport), polymer electrolytes always end up with an undesired low ionic conductivity [6]. Therefore, it becomes a challenge to overcome this limitation and bring about desirable higher conductivity at ambient temperature. Molecular dynamics (MD) simulations, based on the molecular level understanding of the interactions between polymer and ions, may assist in achieving this objective.

Most previously reported MD simulation studies were carried out on PEO/salt or PEO aqueous solutions and provided valuable information on binary mixtures [2–5, 7–9]. Li^+ ions in aqueous solution have a reported limiting

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molar conductivity around $38.76\,\mathrm{Scm^2\,mol^{-1}}$ [10]. Recent experiments discovered that ternary mixtures with water could produce systems with even more attractive properties than binary polymer/salts complexes. Neutron diffraction by isotropic substitution (NDIS) experiments found that addition of water into polymer electrolytes (PEO/LiI) solution dramatically changed the environment of the cation with more ions associating with water than with polymer, not as in the binary solution where cations associated with the polymer chain [11]. These structural changes clearly indicate that water exerts a strong influence on the coordination between cations and ether oxygen. A number of different authors reported the effect of water on diffusion and ionic conductivity of SPEs by NMR spectrometry experiments [12,13]. They found increased ionic conductivity of polymer/salts electrolytes with increased relative humidity. A typical solid polymer electrolyte has conductivity around 10^{-4}–10^{-5} S/cm at room temperature [1]. But after hydration the conductivity could increase as much as 1000 times [12]. Cations decoupling from formerly bonded polymer chains and coordinating to water may account for the increased conductivity, which is consistent with the observed structural change seen in neutron scattering experiments [11–13]. To further investigate the potential development of aqueous solutions of SPEs and understand the role of water molecules, we employed MD simulations to describe the environment of cations in the PEO aqueous solution by calculating radial distribution functions and the coordination numbers of lithium ions. In order to accurately represent intermolecular interactions, we take into account polarizabilty in our simulation force field via the dynamic shell model [14]. In section 2, we explain the simulation model, methodology and potential functions used. In section 3, we present and discuss the simulation results of structural properties and compare them to experimental data. Final conclusions are given in section 4.

2. MD simulations

2.1 Forcefield

Polarizabilty, the electron redistribution caused by an external electric field, plays an important role in determining structural and dynamic properties of SPEs, as has been shown in previous MD simulation studies of PEO/LiI mixture by Smith and coworkers employing an effective parameterized two-body polarizable forcefield [4,15]. Their work illustrated the significance of polarization effect in the interactions between ions and polymer by comparing distribution functions from their simulations with those obtained from neutron scattering experiments. The best agreement comes from the simulation with a forcefield that includes effective polarizability, whereas predictions from a non-polarizable model were not satisfactory due to the underestimation of interactions between ions and PEO polymer yielding lower ether oxygen coordination number around Li^+ [4]. In addition to the demonstrated importance of polarization effects in PEO/Salts mixture, the induced dipole of water, the third component in our simulated system, in the liquid phase can be as large as 50% of the permanent dipole, as has been pointed out by previous research [16]. Therefore, a crucial step for simulations relies on the accurate inclusion of the polarizabilities. Since the implementation of many-body polarization effect is computationally very intensive for polymer systems, we propose a more efficient approximation of interactions by using the dynamic shell model to include polarizabilties into force fields, and test their accuracy by comparison with experiments.

The total energy, U^{TOT}, of the system is computed as the sum of nonbonded interactions, U^{NB}, defined as the interactions between atoms of different molecules or atoms of the same molecule separated by three or more bonds, bonded interactions (chemical bonds, valence angles and dihedral angles) U^{BOND}, and polarization energy, so that

$$U^{\mathrm{TOT}}(r) = U^{\mathrm{NB}}(r) + U^{\mathrm{BOND}}(r) + U^{\mathrm{POL}}(r) \tag{1}$$

The induced dipole moment $\vec{\mu}$ is given by equation (2):

$$\vec{\mu} = \alpha \vec{E} \tag{2}$$

where $\vec{E}$ and α denote electric field and atomic polarizability ($\mathring{\mathrm{A}}^3$), respectively. Note that this is a simplified version of the more general case, in which polarizability is a tensor; here it is a scalar, corresponding to isotropic polarizability. The polarization energy can be represented by the dynamic shell model [14,17], also known as the adiabatic shell model, which introduces polarizability by splitting an atomic site into a heavy core and a lighter shell connected by a harmonic spring characterized by force constant k [14,17]. The polarizability is then defined as

$$\alpha = \frac{q_{\mathrm{s}}^2}{k} \tag{3}$$

where q_{s} is the charge of the shell. The total atomic charge is then recovered as the sum of the charge of the core, q_{c}, and shell, q_{s} charges. Core-shell units can be thought of as being similar to a diatomic molecule with a harmonic bond, and no Coulombic interaction between the core and shell of the same atom. The induced dipole is given by the core and shell charges and their mutual distance. The polarization energy is given by the energy of the core-shell spring [14,17]:

$$U^{\mathrm{POL}} = \frac{1}{2} k r^2 \tag{4}$$

The non-bonded part of the polymer potential functions consists of Columbic and van der Waals interactions, the latter represented by the Buckingham potential, written as [18,19],

$$U_{ij}^{\mathrm{NB}}(r) = A_{ij} \exp(-B_{ij} r) - \frac{C_{ij}}{r^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r} \tag{5}$$

Table 1. Polarizabilities and partial charges for atoms [17,19].

Atom type	*Atomic polarizability α_i (Å^3)*	*Charge $q_i \times e$*
C1(ether)	1.874	− 0.1187
C(ether)	1.874	− 0.0326
O(ether)	0.748	− 0.2792
Li	0.024 (can be ignored)	1
I	10.042	− 1
O(water)	1.44	− 0.6690
H(water)	NA	0.33450

Note: C1 denotes a carbon atom located at the end of PEO polymer chains.

where A_{ij} and B_{ij} are repulsion parameters; C_{ij} is dispersion parameter. The values of A_{ij}, B_{ij} and C_{ij} used in this work are taken from the force field developed by Smith and coworkers [18]. Short range van de Waals interactions are usually placed only at shells alone.

The water–water intermolecular interactions are modeled by the polarizable simple point charge model (PSPC), consisting of three atomic interaction sites, with Lennard–Jones (LJ) centers and a polarizable center placed on the oxygen sites [19]. All ions were represented by point charges with a LJ center and corresponding parameters were referred to Dang *et al.* [20,21]. Among the ions, polarizability was only assigned to iodide ions since lithium cations are almost non-polarizable ($\alpha_{\mathrm{Li}} = 0.024$ Å^3 [15]). The polarizability of iodine ($\alpha_{\mathrm{I}} = 10.042$ Å^3) is in a good agreement with the MP2 value for I^- calculated from the I[4sp3d]ECP basis set [15]. Atomic charges and polarizabilties used in the presented forcefield are listed in Table 1, and LJ parameters for pairs of the same atom types are listed in Table 2. To derive the parameters of the remaining interactions, we used the Lorentz–Berthelot combining rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \qquad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}. \tag{6}$$

Comparing predicted total distribution functions to those obtained from neutron experiments, we found that contact peaks corresponding to ion–water and ion–polymer interactions were systematically at shorter distances, signaling underestimated repulsions. Therefore, we proceeded by rescaling the repulsive part of the LJ potential so that the structure of the binary polymer mixtures corresponded to available experimental data. This procedure is analogical to the way the PSPC [19] potential was derived from its nonpolarizable potential model (SPC) by rescaling the repulsive part of the noncoulombic interactions.

Table 2. LJ potential parameters.

Atom pairs	*ε_{ij} (Kcal/mol)*	*σ_{ij} (Å)*
C–C	0.082	3.379
O(ether)–O(ether)	0.175	2.846
H–H	0.0085	2.827
Li–Li	0.165	1.506
I–I	0.1	5.167
O(water)–O(water)	0.1295	3.263

Note: the LJ parameters for PEO–PEO interactions were only listed so that the combining rules can be applied for cross interactions; The Buckingham potential was used in the PEO–PEO interactions.

2.2 Simulation methodology

In accordance with the corresponding NDIS experiments [11], the simulated system consisted of six deuterated PEO polymer chains with 12 repeated units, i.e. D—(CD$_2$-—O—CD$_2$)$_{12}$—D (MW = 580), 77 pairs of lithium iodide, and 499 PSPC water molecules (D_2O). The ratio of ether oxygens to cations (EO/Li) was thus approximately 1:1. Using deuterated PEO and water provides insights into the normal polymer and water; results are considered to be valid also for the non-deuterated system, since the properties of heavy hydrogen atoms have little influence on the structural properties of systems. Simulations were carried out in the NVT ensemble using the Berendsen thermostat [17] to maintain the system at temperature 298 K and density 1.6 g/cm^3, which corresponds to a cubic box of length 28.5 Å [11]. We used the cubic periodic boundary conditions. Long-range Coulombic interactions were calculated by employing the Ewald summation method. All chemical bonds were constrained to their equilibrium lengths by the SHAKE algorithm. For computational efficiency, nonbonded interactions were cut off at an intermolecular distance of 10 Å. The system was equilibrated for 1 ns and production runs spanned at least 0.5 ns. Considering the light mass of shell sites, to properly integrate the equations of motion of the system including the shell model for polarizabilities, the multiple time step method was used, with the time step set to 0.1 fs and long range forces recomputed every four time steps. The MD software DL_POLY_2 [17], modified to be consistent with the functional form of the torsional potential used in the current work, was used to perform all simulations.

3. Results and discussion

In this section, we begin by presenting the structure of atoms around ions in the ternary PEO/LiI/H_2O solutions at room temperature by calculating the distribution functions and coordination numbers. We then compare them to NDIS results [11].

Neutron scattering experiments measure the total structure factor, which can be decomposed into contributions $S_{\alpha\beta}$ of atom types α and β. These partial structure factors are related to the pair distribution function, $g_{\alpha\beta}(r)$, through the Fourier transform:

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^\infty r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} \mathrm{d}r, \tag{7}$$

where r is the distance between atoms α and β, and Q is the magnitude of the momentum transfer.

To directly connect the simulations and experiment, we calculate the total distribution function for all the atoms around a lithium ion, $G_{\mathrm{Li}}(r)$, which is defined as [11]:

$$G_{\mathrm{Li}}(r) = \frac{A}{S} g_{\mathrm{LiO}}(r) + \frac{B}{S} g_{\mathrm{LiD}}(r) + \frac{C}{S} g_{\mathrm{LiC}}(r) + \frac{D}{S} g_{\mathrm{LiI}}(r) + \frac{E}{S} g_{\mathrm{LiLi}}(r) \tag{8}$$

The coefficients A, B, C, D are related to atomic number density c_i and neutron scattering length b_i as shown in the following equations [11]:

$$A = 2c_{\mathrm{Li}} c_{\mathrm{O}} b_{\mathrm{O}} \delta b_{\mathrm{Li}} \tag{9}$$

$$B = 2c_{\mathrm{Li}} c_{\mathrm{D}} b_{\mathrm{D}} \delta b_{\mathrm{Li}} \tag{10}$$

$$C = 2c_{\mathrm{Li}} c_{\mathrm{C}} b_{\mathrm{C}} \delta b_{\mathrm{Li}} \tag{11}$$

$$D = 2c_{\mathrm{Li}} c_{\mathrm{I}} b_{\mathrm{I}} \delta b_{\mathrm{Li}} \tag{12}$$

$$E = c_{\mathrm{Li}}^2 \left(\left(b_{\mathrm{Li}}^6\right)^2 - \left(b_{\mathrm{Li}}^{\mathrm{nat}}\right)^2 \right) \tag{13}$$

$$S = A + B + C + D + E, \tag{14}$$

where δb_{Li} is the difference between the scattering length for lithium with the natural abundance ($b_{\mathrm{Li}}^{\mathrm{nat}}$) and the one enriched in ^{6}Li (b_{Li}^6) [11].

Figure 1 shows the comparison of the total distribution function around lithium ions, $G_{\mathrm{Li}}(r)$, between our MD simulations and the NDIS experiment [11]. Both of them exhibit the first two peaks located at 1.95–1.98 and 2.62–2.66 Å, identified as the distributions of oxygen and hydrogen atoms of the nearest-neighbor water molecules, respectively. Previous reported simulations of aqueous inorganic solutions, such as LiCl in water, found very similar peaks located at 1.96–2.12 for Li-O and 2.52–2.61 Å for Li-D [11,22,23]. To calculate the number of water molecules in the first coordination shell of Li$^+$, we followed [11] and integrated the total distribution function from 1.5 to 3.0 Å, covering thus the first two peaks. We found the same number of 3.2 in both simulation and experiments. Studies of aqueous inorganic solutions with similar ratio of water molecules to cations yield similar solution structure around the Li ion, suggesting that the PEO in PEO/LiI/water solutions does not have a large influence on the hydration of Li ions [11,22,23]. Both MD simulation and experiments thus suggest that in the ternary SPEs solution more lithium ions are found to decouple from the polymer chain and are in close proximity to the water oxygen [11].

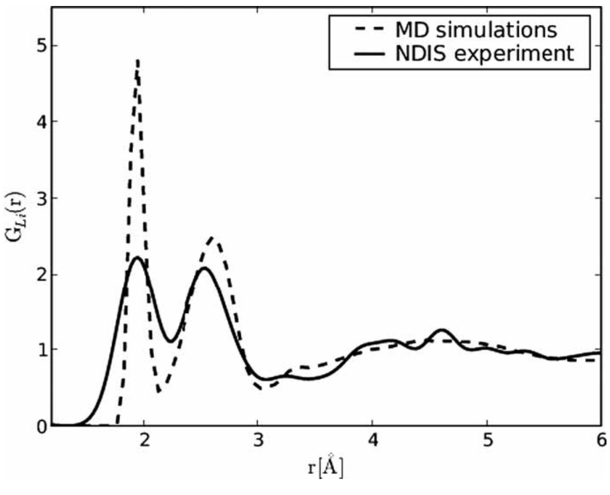

Figure 1. Total distribution function for lithium ions, G_{Li}. Comparison of MD simulations (dashed line) with experimental results [11] (solid line).

To obtain more detailed insight into the ion environment, we also directly calculated the Li$^+$ water oxygen pair distribution function and its integral according to

$$N(R) = 4\pi\rho_\alpha \int_0^R r^2 g_{\mathrm{Li}\alpha}(r)\mathrm{d}r, \tag{15}$$

where ρ_α is the number density of water oxygens. Both results are shown in figure 2. The analysis shows that there are 3.6 water molecules within the first hydration shell ($r < 2.5$) and the remaining valence is saturated by the average of 0.3 ether oxygens and 0.1 I$^-$ anion. Li$^+$ ions are thus in a very similar environment as in pure water. As our complementary simulations has shown, Li$^+$ ions in binary PEO/LiI melt are surrounded by 3.5 ether oxygens and the remaining valence is saturated by 0.5 I$^-$ counter ions. Addition of water breaks most of these bonds, saturating the cation valence. Freed up ether oxygens form on average 1.6 H-bonds with water hydrogens that provide oxygens almost tetrahedral environment. These interactions are documented in figure 3 of the ether oxygen–water hydrogen distribution function and its integral computed according to (15). The hydration of PEO/LiI mixture also results in the straightening of polymer chains, which are no longer curled around Li$^+$ ions. These changes, along with the separation of cation–anion pairs, are most likely behind the observed substantial increase of ionic conductivity. The coordination numbers of Li$^+$ ions in binary and ternary mixtures are summarized in Table 3 along with diffusivities of Li$^+$ ions in these environments. We can notice that in the studied ternary mixture most cations are surrounded by water, but the ratio of different ligands in the first coordination shell roughly corresponds to the ratio of concentrations of these atoms.

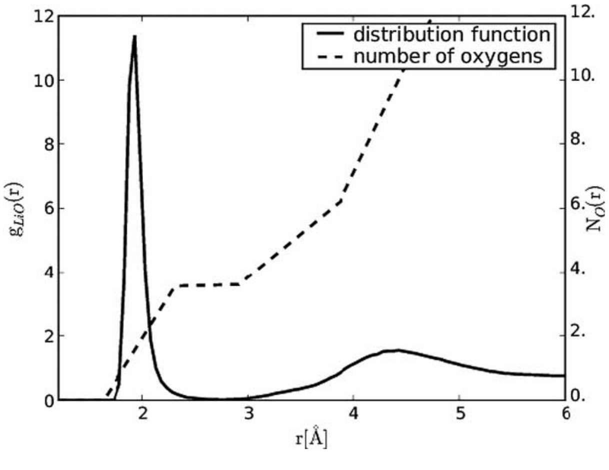

Figure 2. Li$^+$ ion–water oxygen pair distribution function, $g_{\mathrm{LiO}}(r)$, (solid) and its integral, $N_{\mathrm{O}}(r)$, (dashed) from MD simulations.

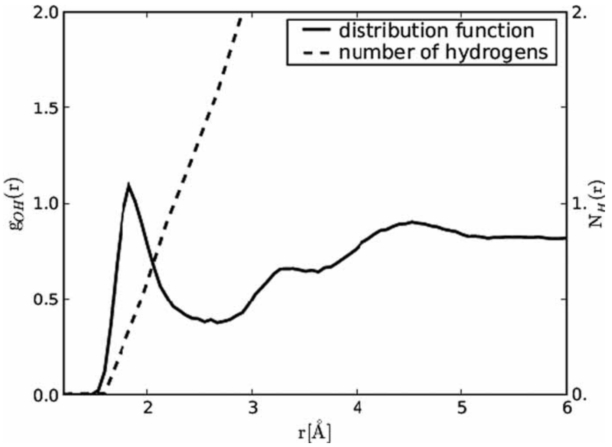

Figure 3. Ether oxygen–water hydrogen pair distribution function, $g_{\mathrm{OH}}(r)$, (solid) and its integral, $N_{\mathrm{H}}(r)$, (dashed) from MD simulations.

Table 3. Lithium coordination numbers and diffusivities in different mixtures.

Ligands	*Water/LiI (6.4:1)*	*PEO/LiI (5:1)*	*PEO/Water/LiI (0.9:6.5:1)*
Water oxygen	4.0	NA	3.6
Ether oxygen	NA	3.5	0.3
Iodide	0.0	0.5	0.1
Diffusivity × 10^8 [m^2/s]	0.0505	0.0002	0.012

Note: Numbers in parentheses give the ratios of appropriate ligands in the mixture.

The simulations thus suggest that while water successfully competes with other ligands, modifies lithium environment, and changes the structure of polymer, at low water concentrations, which are more interesting from the practical point of view, Li^+ will be still under a strong influence of PEO ether oxygens. Further analysis shows that most lithium ions in our ternary mixture are coordinated by four water oxygens but some of them are coordinated by three or four ether oxygens. Mixed coordination shells are rare. The relative success of PEO in the complexation of lithium ions can thus be ascribed to the chelate effect, which stabilizes the complexes despite weaker interactions of individual ether oxygens. As for the diffusivity of Li ions, we may notice that while it is approximately 50 times larger in the ternary mixture than in the pure polymer, it is only about 1/4 of the value in pure water. Since most ions are surrounded by water, the results suggest that polymer molecules still inhibit the dynamics of ions by constraining the whole aqueous environment and fixing it through hydrogen bonds between ether oxygens and water hydrogens.

4. Conclusions

The MD simulation results presented here have shown that adding low concentration of PEO polymer molecules to lithium-salt aqueous solution does not considerably influence the hydration of lithium ions, with most of them still coordinated to water. This can be explained by high solubility of ions in water as a result of its high dielectric constant. This finding agrees well with previous experimental research on the PEO/salt and PEO/water mixtures. It was also found that despite relatively weaker interaction between ions and ether oxygens, PEO can still compete with water due to the stabilizing chelate effect. The interesting structural changes in both ion complexation and polymer structure upon addition of water may bring about a desired higher ionic conductivity because of the increased mobility of ions after the decoupling of cations from polymer and separation of ion pairs. As a next step in our study, we will consider systems with lower water concentrations so that we can directly relate our simulations to available experimental measurements of ionic conductivity.

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