

A comparison of Li^+ transport in dimethoxyethane, poly(ethylene oxide) and poly(tetramethylene oxide) by molecular dynamics simulations

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Abstract

Pure dimethoxyethane (DME), poly(ethylene oxide) (PEO) and poly(tetramethylene oxide) (PTME) and their binary mixtures with LiI were investigated by molecular dynamics simulations (Li/O proportion equal to 1:8). The properties analyzed included the relative occurrence of *trans* and *gauche* population for selected torsions, radial distribution functions, mean square fluctuations and mobilities. We studied the relation between the ionic transport process of Li^+ and the conformational behavior in DME, PEO and PTME systems. We investigated the solvation shell around Li^+ in those systems. The *gauche* effect of DME and PEO (OCCO torsion) is strongly related to salt addition. This effect is more pronounced in DME-based systems. Li^+ /O coordination occurs in all considered systems. The mobility of the ionic species is larger in DME than in the polymers. In PTME, it is only slightly smaller than in PEO. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolytes; Molecular dynamics simulation; Poly(ethylene oxide); Poly(tetramethylene oxide)

1. Introduction

The most widely studied polyether is poly(ethylene oxide) (PEO), at the same time, it is the standard host polymeric matrix for dissolving inorganic salts. In this work, we study the mechanism for Li^+ transport through this polymer and its relation to local structure and dynamics through molecular dynamics simulations. We also investigate two other polyethers: 1,2-dimethoxyethane (DME) as a prototype system for

PEO, and poly(tetramethylene oxide) (PTME) as a possible alternative polymer electrolyte.

The investigation of conformational and structural characteristics of DME has been the subject of exhaustive studies in the last two decades, both experimental and theoretical, and in both the gas phase and condensed phases [1–4]. Despite of all the investigations, the conformational preferences of DME are still a controversial subject [5], mainly due to the *gauche* effect: polar substituents (here oxygen) in 1,2-positions result in *gauche* conformations around C–C bonds.

PTME and its mixtures with salts have been explored as an alternative host polymer, and their use is still controversial. It was shown by Alamgir et

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al. [6] that the conductivities at room temperature are lower than in similar PEO systems. Mendolia and Farrington [7], on the other hand, measured nearly equal conductivities for poly(tetramethylene glycol) PTMG/CoBr₂ (10^{-7} S/cm) and poly(ethylene glycol) PEG/CoBr₂ (10^{-7} S/cm). They found spectroscopic evidence suggesting that the poor conductivities are a consequence of low concentration of charge carriers. Furtado et al. [8] investigated both PTMG/LiClO₄ and PTMG/PEG/LiClO₄ systems and found that the conductivity values measured at room temperature do not vary significantly (below 10^{-4} S/cm for compositions around Li⁺/O=1:100 to 1:4) and the highest value measured was found for the copolymer at Li⁺/O=1:6 (2.2×10^{-3} S/cm). In a recent paper, Ferreira et al. [9] studied theoretically the behavior of selected polyethers (20 monomeric units), and it was shown that PTME has similar structural properties as PEO. Thus, PTME-based systems could be, a priori, similar to PEO systems.

The present work aims to understand the similarities and differences between the three systems: DME, PEO and PTME, and their mixtures with LiI. We also try to relate observed values of the ionic mobilities to structural features of the polymeric hosts.

2. Methodology

The molecular dynamics investigations of the conformational and structural properties of pure DME were done using 125 DME molecules, starting from the molecules on lattice positions and allowing them to relax to a liquid structure in 300 ps. The polymers were constructed with the RIS model [10–12] and the number of monomeric units (n) was $n=400$ for PEO and $n=250$ for PTME in order to obtain similar molecular weights. Experimentally, it is well-known that the highest Li⁺ conductivity is reached at Li/O proportion equals to 1:8 [13]. Thus, this proportion was used in all systems to simulate the electrolyte, the anion being I⁻. We also performed simulations with Li/O proportions equal to 1:4, 1:16 and 1:32 for the DME-based system in order to investigate the influence of salt concentration. The ions were inserted into equilibrated host systems at random positions, after which a further 1500 ps of equilibration (pure polymer) was performed.

All the analyses were performed after the system reached equilibrium (density convergence). The total time of the simulations at the equilibrium state was $t=1500$ ps. The molecular dynamics time step was 2 fs, constant temperature ($T=330$ K) and pressure ($p=101.3$ bar) were maintained by using the Berendsen thermostat and manostat with coupling times of 1.0 ps (T) and 2.0 ps (p), respectively. We used the force field previously developed for LiI in poly(ethylene oxide) [15–17] and for PTME [18,19] with the following modifications (for notation of the force field terms, see Ref. [14]): bond distances were constrained by the SHAKE method and nonbonded interactions were cut off at 1.1 nm. Beyond the cutoff, a reaction field correction with dielectric constants of $\epsilon_{\text{RF/DME}}=7.6$, $\epsilon_{\text{RF/PEO}}=3.6$ and $\epsilon_{\text{RF/PTME}}=3.0$ were applied. Configurations were saved for the analysis every 15 ps. All calculations were done with the YASP program [14].

3. Results and discussions

DME and PEO have two distinct types of dihedral angles involving only heavy atoms: CCOC (and the symmetry-equivalent COCC) and OCCO. CCOC torsions are predominantly in the *trans* ($\sim 180^\circ$) conformation. The relative occurrence of the *trans* conformation is practically independent of the salt

Table 1
Relative occurrence of the *trans* population for selected torsions in DME, PEO and PTME systems (equilibrium state, 330 K)

| Relative occurrence of <i>trans</i> population in DME torsions/(%) | | | | | |
|---|------|------|------|------|------|
| Torsion/Li:O proportion | Pure | 1:32 | 1:16 | 1:8 | 1:4 |
| CCOC | 76.6 | 76.9 | 76.2 | 76.8 | 78.8 |
| OCCO | 31.5 | 28.2 | 23.7 | 22.1 | 21.0 |
| Relative occurrence of <i>trans</i> population in PEO torsions/(%) | | | | | |
| Torsion/Li:O proportion | Pure | 1:8 | | | |
| CCOC | 86.0 | 84.8 | | | |
| OCCO | 41.4 | 35.0 | | | |
| Relative occurrence of <i>trans</i> population in PTME torsions/(%) | | | | | |
| Torsion/Li:O proportion | Pure | 1:8 | | | |
| CCOC | 91.4 | 85.9 | | | |
| CCCC | 84.5 | 80.5 | | | |
| CCCO | 71.1 | 65.4 | | | |

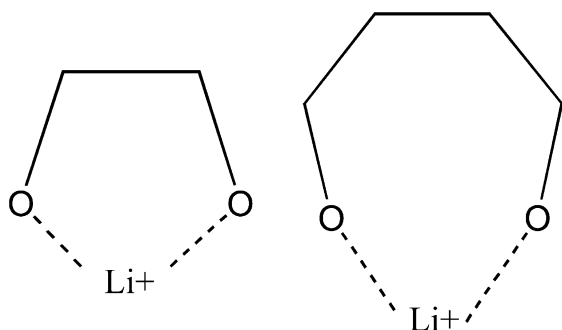


Fig. 1. Conformational behavior for PEO and PTME systems to coordinate Li^+ ion.

concentration (Table 1). In contrast, the central OCCO dihedral of DME is predominantly *gauche* ($\sim \pm 60^\circ$). This is the well-known *gauche* effect of the ethylene-1,2-diether motif, also present in poly(ethylene oxide). The population of the *gauche* state increases with salt addition. The effects of LiI addition to DME are similar to what was found previously for poly(ethylene oxide) [15]. Also there, the OCCO dihedrals showed a marked increase of *gauche* population with salt addition, whereas the CCOC dihedrals were basically unaffected by the salt. It means that the OCCO torsion and its conformational behavior are strongly dominated by the *gauche* effect, which, in turn, is influenced by the salt concentration. It also means that this torsion is important in the process of Li^+ co-ordination by DME and PEO.

PTME has three types of dihedral angles involving heavy atoms only, CCCC, CCCO (and OCCO) and

Table 2

Number of neighbors and distances around Li^+ in the first solvation shell for DME, PEO and PTME systems considering $\text{Li}-\text{O}$, $\text{Li}-\text{I}$ and $\text{Li}-\text{Li}$ pairs (after equilibration, 330 K)

| Distance/nm | Li^+ pair | 1:31 | 1:16 | 1:8 | 1:4 |
|-------------|---------------------|------|------|------|------|
| 0.25 | O/DME | 2.15 | 1.51 | 1.51 | 1.10 |
| | O/POE | | | 1.17 | |
| | O/PTME | | | 1.18 | |
| 0.53 | Li^+ /DME | 1.70 | 4.80 | 4.66 | 6.07 |
| | Li^+ /POE | | | 6.09 | |
| | Li^+ /PTME | | | 0.53 | |
| 0.33 | I^- /DME | 2.09 | 2.76 | 2.84 | 3.06 |
| | I^- /POE | | | 3.09 | |
| | I^- /PTME | | | 1.94 | |

Distance refers to the radius to which the corresponding RDF is integrated. This is equivalent to the first minimum of the corresponding RDF.

CCOC (and COCC). All of these are predominant in the *trans* ($\sim 180^\circ$) conformation, with or without added LiI (Table 1). Surprisingly, the salt addition has a small but noticeable influence on the relative occurrence of the PTME torsions: for all of them, *trans* decreases: $\sim 6\%$ for CCOC, $\sim 4\%$ for CCCC, and $\sim 8\%$ for CCCO. It is clear that such influence is much slighter than the one observed in OCCO torsion in PEO and DME, as the *trans* population is still dominant. However, it suggests that the polymer changes its conformation in order to acquire a structure that allows a more effective complex formation with Li^+ . The *gauche* conformation is probably not reached because of the steric effects (the long distances between the oxygen atoms increase the tension

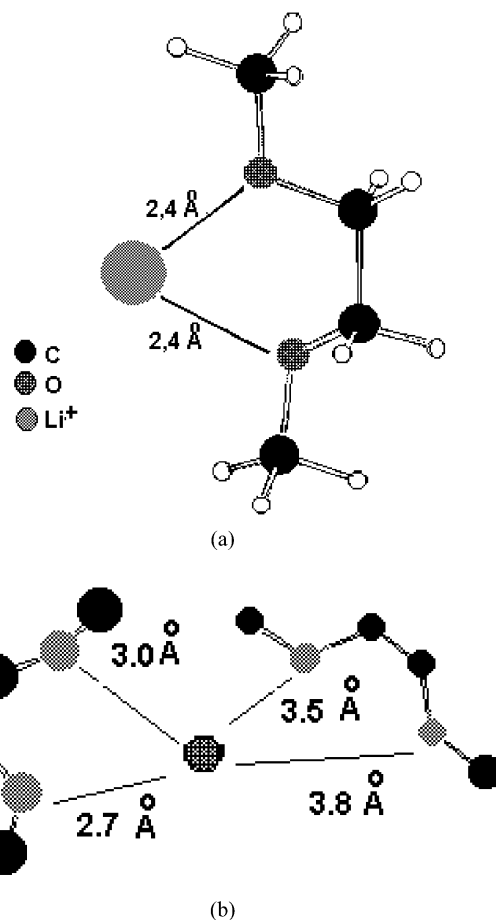


Fig. 2. Li^+ and DME complexation with one (a) and two (b) DME molecules (proportion Li/O equals to 1:16).

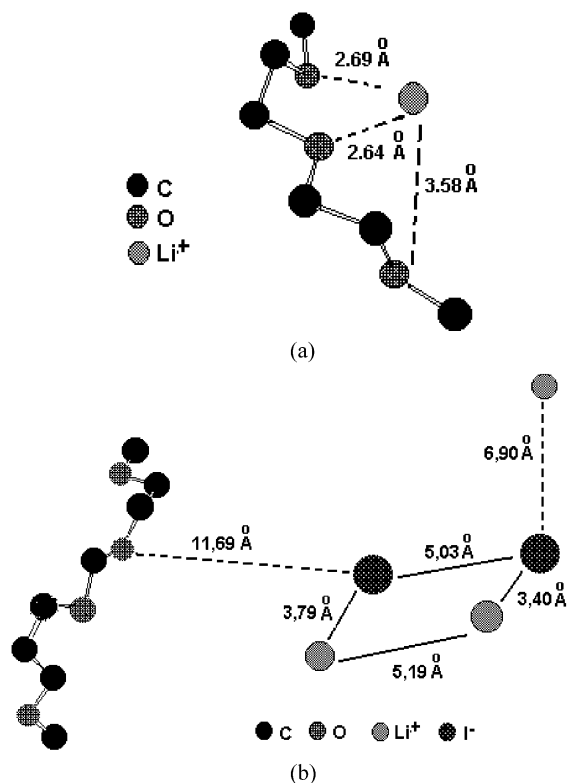


Fig. 3. Local structure of Li^+ complexation with PEO (a) and both PEO and ions (b).

of the formed structure to complex the cation in long polymer chains). Fig. 1 sketches the conformational structures necessary for PEO and PTME to be able to co-ordinate the Li^+ ion.

In order to obtain the information about local structure, such as complex formation and ion interactions, the appropriate radial distribution functions $g(r)$ of Li^+ with other atoms (O, I, and other Li) were calculated and integrated to calculate the number of neighbors of each type. The solvation shells around Li^+ for DME, PEO and PTME systems are summarized in Table 2. The number of co-ordinated oxygen decreases in DME with salt addition and the number of co-ordinated ions increases. The reduction of O neighbors from ~ 2 to ~ 1 in DME suggests that either DME can act as a monodentate ligand and/or part of DME acts as a bidentate ligand and part of DME has no Li^+ contact at all (Fig. 2). The number of ions around Li^+ obviously increases with salt concentration and it possibly leads to a phase separa-

tion at higher salt concentration. Moreover, the number of co-ordinated oxygen is larger in DME than in either polymer. This is not surprising, as the DME is a small molecule and can adopt a structure suitable for co-ordinating the Li^+ easier than a macromolecule can.

The analysis of the polymer-borne systems shows that the co-ordination of the ions in PEO is unusually high. It suggests at least ion clustering, and possibly a phase separation. The low number of oxygen atoms around Li^+ ion suggests that the polymer acts, on average, as a monodentate ligand. However, higher co-ordinations are found as well (Fig. 3a) and they agree with previous simulations. The function $g(r)$ is a descriptor most appropriate for homogeneous ion distributions, where the local distribution does not change through the system and the whole system has the same behavior as the local structure. In the case of clustering in polymer electrolytes (cf. Fig. 3b), the ion distribution is not homogeneous and the whole system is not a reflection of the local structure. As it averages the structure over heterogeneities, the $g(r)$

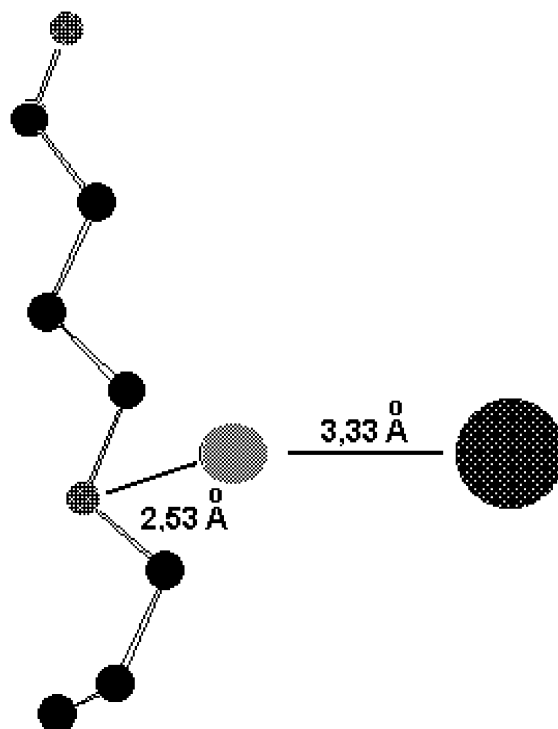


Fig. 4. Local structure of Li^+ complexation with PTME.

Table 3

Mobility (root mean square fluctuation in nm at 1 ns) for ions in DME, PEO and PTME systems

| Li/O proportion | 1:31 | 1:16 | 1:8 | 1:4 |
|-----------------------|------|------|------|------|
| Li ⁺ /DME | 5.50 | 3.54 | 3.42 | 1.80 |
| Li ⁺ /PEO | | | 0.68 | |
| Li ⁺ /PTME | | | 0.28 | |
| I ⁻ /DME | 5.00 | 3.51 | 3.42 | 1.43 |
| I ⁻ /PEO | | | 0.50 | |
| I ⁻ /PTME | | | 0.26 | |

function is not a good property for local structure analysis of the whole system: we could observe PEO acting as a polydentate as well as a monodentate ligand (Fig. 3).

On the other hand, PTME system shows a low co-ordination for both ions, especially Li⁺, which means that there is no indication of a phase separation. It suggests that the ion distribution in PTME is not similar to PEO. The number of oxygen atoms and iodide around Li⁺ suggests that this species is co-ordinated with both O and I⁻ (the average of the co-ordination number is equal to 2), but the co-ordination is stronger with O (cf. Fig. 4).

Trying to understand the process of ionic transport through the considered systems, the time-dependent root mean square fluctuation $\text{RMSF}(t) = \langle x(t) - \bar{x}^2 \rangle^{1/2}$ was calculated. Its value at 1 ns is used as a measure of relative mobility of the ionic species (Li⁺ and I⁻). Proper tracer diffusion coefficients cannot be reported, since their motion is still sub-diffusive on the time scale of the simulation. The mobilities are summarized in Table 3. As expected, the mobility of Li⁺ and I⁻ decreases with the salt concentration in DME-based systems. It seems that the salt addition stiffens the system (increases the viscosity) leading to a low mobility. Mobilities in DME are much larger than in either polymeric system.

The mobility in PEO is larger than in PTME system for both ions. It is well-known that the heteroatom–carbon–carbon–heteroatom sequence is most favorable for cation co-ordination. The larger number of available co-ordination sites in PEO can explain that the Li⁺ transport is faster than in PTME. The mobilities of Li⁺ and I⁻ are similar for all the systems considered. Similar transport numbers for Li⁺ and small anions have also been found in many experiments.

4. Conclusions

We conclude that DME is a good model to understand some PEO properties, mainly the conformational behavior. In both systems, the CCOC (*trans* population is dominant) and OCCO (*gauche* population is dominant) torsion show the same behavior. The *gauche* effect observed for OCCO torsion is stronger in DME system with salt addition. For the PTME system, the *trans* population is dominant for all considered torsions (CCOC, CCCC and CCCO). With salt addition, all torsion populations shift slightly towards *gauche*, thus facilitating the complexation of Li⁺.

The lithium co-ordination is similar in DME and both polymeric systems: the Li⁺ ions can be complexed with a mono- or polydentate ligand. Furthermore, the Li⁺ ions can be complexed by other ions or the polymer chain or both. We observed an indication of ion clustering in for the PEO–LiI system from the behavior of the $g(r)$ function.

Finally, the salt mobility is larger in DME than in either polymer, a typical liquid electrolyte characteristic. The salt mobility in both polymeric systems is similar, being slightly smaller in PTME. Thus, a deeper investigation of PTME-containing systems (pure, blends, copolymers) as an alternative polymer electrolyte could be useful. The study of copolymer PTME/PEO showed that such system has good values of conductivity [8]. It means that some interesting structural and dynamic properties found in PEO and PTME can be enhanced by using both polymers as copolymers.

Acknowledgements

The authors would like to thank the Conselho Nacional de Desenvolvimento Científico (CNPq), the Fundação de Amparo à Pesquisa do Estado de Minas Gerais and the Programa de Apoio ao Desenvolvimento Científico e Tecnológico (PADCT, Proc. No. 62.0241/95.0) for supporting this project.

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