



# Solvation of lithium ion in dimethoxyethane and propylene carbonate



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## ABSTRACT

Solvation of the lithium ion ( $\text{Li}^+$ ) in dimethoxyethane (DME) and propylene carbonate (PC) is of scientific significance and urgency in the context of lithium-ion batteries. I report PM7-MD simulations on the composition of  $\text{Li}^+$  solvation shells (SH) in a few DME/PC mixtures. The equimolar mixture features preferential solvation by PC, in agreement with classical MD studies. However, one DME molecule is always present in the first SH, supplementing the cage formed by five PC molecules. As PC molecules get removed, DME gradually substitutes vacant places. In the PC-poor mixtures, an entire SH is populated by five DME molecules.

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## 1. Introduction

Search for novel and investigation of the existing electrolyte solutions [1–8] in organic solvents constitute a great importance and urgency in the today's physical chemistry and electrochemistry due to the recent emergence of multiple portable devices. Lithium salts [9–12] dissolved in the mixed molecular solvents, such as dimethoxyethane (DME) and propylene carbonate (PC) are applied in the lithium-ion batteries [13–15], since they exhibit wide electrochemical windows and other favorable properties. High ionic conductivity and dielectric constant of the electrolyte solution always arrive at the cost of a high shear viscosity [14]. The compromise can be achieved by mixing highly polar cyclic ethers, such as PC, with low-polar linear ethers, such as DME. Fortunately, these solvents are well miscible with one another giving rise to a variety of compositions. The resulting mixtures provide an electrochemically interesting background for electrolyte systems.

The complexity of experimental setups and molecular-level data interpretations in the case of many-atom molecules considerably hinders development of the efficient electrolyte solutions. The factors determining key properties, such as ion solvation regularities and ion transport regularities, must be clearly understood to foster progress in the lithium-ion batteries. Mixed solvents are challenging for theoretical investigation because of the abundant specific molecular interactions in these systems. The complexity increases

drastically with every new molecular or ionic species added to the mixture.

No consensus still exists in the community regarding the structure of the lithium ion solvation shells in its DME–PC solutions. The coordination number of  $\text{Li}^+$  in the solutions remains actually unknown. Depending on the method of investigation and working approximations, the coordination number is reported anywhere between two and eight [14,16–20]. While the coordination number of eight is unlikely physical due to the size of the solvent molecules, the coordination number of two suggests virtually non-solvated ion in the polar solvent, which is bizarre. Better precision is required to build theoretical descriptions of these ion–molecular systems.

Prezhdo and coworkers [14] have recently reported classical molecular dynamics (MD) simulations to study lithium tetrafluoroborate ( $\text{LiBF}_4$ ) in the pure and mixed cyclic and linear carbonates with various salt concentrations. The additive, non-polarizable force field was applied to describe ion–ionic, ion–molecular, and molecule–molecular interactions in these complex systems at room conditions. They found that  $\text{Li}^+$  is preferentially solvated by a cyclic and more polar co-solvent, suggesting that a strong electrostatic attraction dominates over possible steric hindrances. The coordination number of  $\text{Li}^+$  varies from 5 to 6 depending on the lithium salt concentration [14]. This variation is observed due to formation of ion pairs in the concentrated solutions of  $\text{LiBF}_4$ . Unfortunately, the model applied by these authors does not account for electronic polarization, which definitely occurs in the real-world systems between  $\text{Li}^+$  and oxygen atoms of the co-solvents, especially with those of PC. This con of the interaction model may turn out critical at certain circumstances.

The polarizable model by Borodin and Smith [8] provides the first peak for the Li–O atom pair (in  $\text{LiPF}_6$ –ethylene carbonate)

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near 2.0 Å with a height of 30, which is closer to the result of the *ab initio* molecular dynamics (AIMD) simulation [7] and significantly smaller than the results obtained using the non-polarizable models [14]. The authors suggest that the existing non-polarizable models overestimate binding energy between the lithium-ion and cyclic carbonates. This supposition looks, in general, reasonable due to fixed electrostatic charges employed in the discussed pairwise models. Ganesh and coworkers [7] reported AIMD simulations of ethylene carbonate and propylene carbonate with  $\text{LiPF}_6$  at the experimentally relevant concentrations to build solvation models. These developed models can be used to explain available neutron scattering and nuclear magnetic resonance results and to compare the lithium-ion solvation energies and self-diffusion constants. The Born–Oppenheimer AIMD empowered by the pure exchange–correlation functional was used with specific pseudopotentials in the canonical and microcanonical ensembles. According to these simulations, the coordination number of  $\text{Li}^+$  equals to four [7], which is smaller than the above introduced result (5–6) by Prezhdo and coworkers [14].

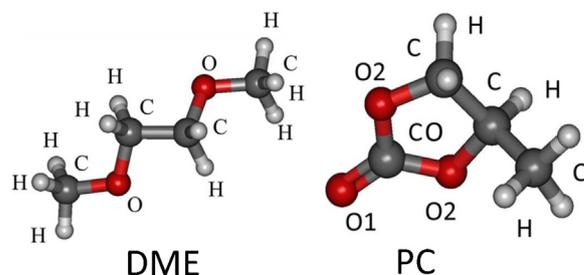
This persisting controversy in literature calls for an additional attention to the problem of  $\text{Li}^+$  solvation in the electrolyte systems. On one side, the AIMD simulations offer a more physically relevant and mathematically sophisticated description of the phenomenon. On another side, the pure density functionals are well-known to overestimate electron transfer, which may result in the underestimation Li-solvent binding energy (in contrast to possible overestimation in the study or Prezhdo et al.) [14]. Furthermore, small systems used in AIMD cannot properly account for a long-range structure, which is important in any ion–molecular system. Finally, the AIMD simulations reported by Ganesh et al. were conducted at 310–400 K. While the coordination number of 4 (Li–O) may be completely relevant at 400 K, it is not fairly clear whether the performed sampling at 310 K is enough to derive properties. Re-organization of the first coordination sphere can require tens of picoseconds at room conditions.

This work contributes the ongoing discussion by performing PM7-MD simulations of a few  $[\text{Li–DME–PC}]^+$  non-periodic systems to investigate (1) structure and composition of the lithium-ion first and second solvation shells; (2) dependence of the lithium-ion coordination number on the DME–PC mixture content; (3) energetics of the lithium-ion binding to both co-solvent molecules. The PM7-MD method [21–23] provides a comprehensive tool offering an electronic-structure description of every system. Thanks to intelligently parameterized integrals in PM7 [24–27], PM7-MD performs better than density functional theory powered AIMD simulations in the sense of computational cost. Unlike pure density functional theory, PM7 does not have a reputation of a method that overestimates an electron transfer. Nevertheless, comparison with the experimental data, where available, is desirable.

## 2. Methodology

The PM7-MD simulations [21–23] were performed using the three systems (Table 1) featuring mixtures of propylene carbonate and dimethoxyethane. All simulations were performed at 300 K with temperature maintained constant using weak coupling to the external thermal bath [28].

The PM7-MD method obtains forces acting on every atomic nucleus from the electronic structure computation using the PM7 semiempirical Hamiltonian [24–27]. PM7 is a parameterized Hartree–Fock method, where certain integrals are pre-determined based on the well-known experimental data, such as ionization energies. This solution allows for effective incorporation of the electron–correlation effects, while preserving a quantum-chemical



**Figure 1.** Optimized chemical structures of dimethoxyethane and propylene carbonate molecules. The geometry optimizations were carried out using the EF algorithm and the wave function was constructed using the PM7 Hamiltonian approximation. These designations of atoms will be used throughout the paper to discuss the simulated systems.

nature of the method. Therefore, PM7 is able to capture any specific chemical interaction. On the contrary, classical pairwise interaction potentials are unable to represent formation/destruction of the covalent bonds, whereas formation/destruction of the hydrogen bonds can be modeled using point electrostatic charges. PM7 is more physically realistic than empirical force field techniques. Note that PM7 includes an empirical correction for the dispersive attraction. Thus, it can be successfully used to model hydrocarbon moieties. The accuracy and robustness of the PM7 parameterization, as applied to thousands of versatile chemical systems, was demonstrated by Stewart elsewhere [24–27].

The derived forces are coupled with the initial positions of atoms and randomly generated velocities (Maxwell–Boltzmann distribution). Subsequently, Newtonian equations-of-motions can be constructed and numerically integrated employing one of the available algorithms. This work relies on the velocity Verlet integration algorithm. Due to rounding errors and other numerical inaccuracies, total energy of the system is not perfectly conserved, as in any other MD simulation method. Temperature may need to be adjusted periodically by rescaling atomic velocity aiming to obtain the required value of kinetic energy with respect to the number of degrees of freedom. This work employs a weak temperature coupling scheme with a relaxation time of 50 fs, whereas the integration time-step equals to 0.5 fs. This integration time-step is set based on the preliminary benchmarks on proper energy conservation (using molecular dynamics simulations in the constant-energy ensemble).

More details of the present PM7-MD implementation are provided elsewhere [21–23]. The interface between PM7 and molecular dynamics has been implemented by means of ASE (Atomistic Simulation Environment) [29]. The method has been successfully applied to address problems of ionic liquids [21,22] and nanoparticles [23]. Local structure of the liquid-matter ion–molecular systems was characterized using a set of pair correlation functions (PCFs). The PCFs were calculated using simple in-home tools along the sampling stage of each PM7-MD trajectory (Table 1). Prior to quantum-chemical analysis, geometries of systems I, II, and III were optimized using the eigenfollowing (EF) algorithm (implemented in MOPAC2012 in the improved form) [27]. The initial geometries of all simulated systems were constructed in Gabedit ver. 2.4 [30]. This software was also employed to produce molecular images (Figs. 1 and 2) based on the snapshots in Protein Data Bank format.

Supplementary Information contains comparison between  $[\text{Li+DME+PC}]^+$  structure using density functional based Born–Oppenheimer molecular dynamics and PM7-MD. The performed numerical comparison indicates satisfactory performance of PM7-MD for the problem of interest.

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