

## Simulation Studies of Ions in Ethylene Carbonate

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**Abstract:** Molecular dynamics computer simulations are used to examine the thermodynamic and structural properties of ions in an ethylene carbonate solution. Parameters optimized to reproduce experimental solvation free energies are developed and the solvation structure of the ions is determined. The simulation data indicates the ethylene carbonate molecules have stronger direct interactions with the cations than with anions.

**Keywords:** Ions, Molecular Dynamics, Free Energies, Ethylene Carbonate

### 1. Introduction

Ethylene carbonate (EC, see Figure 1) is a polar, aprotic solvent and a good solvent for ions. These properties make it a good solvent for lithium batteries.<sup>1,2</sup> Molecular level computer simulations are a useful tool for understanding these materials. These methods require a potential energy function, or force field, which is characterized by a set of parameters. Optimally, parameters developed for one system with a particular composition, temperature and pressure could be transferred to another. There has been significant effort in developing potentials for aqueous systems, in which the parameters are optimized to reproduce experimental values for thermodynamic, structural and transport properties. In using these parameters for non-aqueous systems some parameters may require adjustment to achieve an accurate model.<sup>3</sup> Here we present calculations of the free energy of solvation for a series of monatomic, monovalent ions (four halide anions and the potassium cation) in EC, for which there is directly comparable experimental data.<sup>2</sup> We then present parameters optimized against this data and use the optimized parameters to study the ionic solutions.

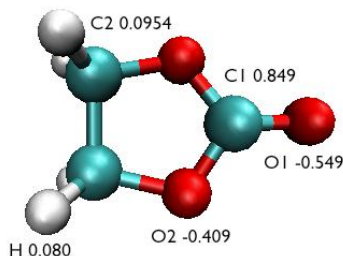


Figure 1. Ethylene carbonate showing atom labels and charges.

### 2. Methods

The interactions between the particles are taken to be a combination of Lennard-Jones and Coulombic terms so that the interaction between two (non-bonded) atoms  $i$  and  $j$  is given by  $E_{ij}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}$

where  $r_{ij}$  is the distance between the atoms,  $q_i$  is the charge of atom  $i$ , and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the Lennard-Jones parameters for  $i$  and  $j$ . This level of molecular interactions, including as it does excluded volume (the  $r^{-12}$  term), dispersion ( $r^{-6}$ ) and Coulombic interactions ( $r^{-1}$ ), can be thought of as a minimal description and is commonly used in molecular simulations. More complicated potentials can include polarizability and charge transfer, among other terms. The Lennard-Jones parameters for atoms of different types are determined from combining rules, in this study, the Lorentz-Berthelot rules are used,  $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$  and  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ . For each atom type, this gives three parameters ( $\epsilon_i$ ,  $\sigma_i$  and  $q_i$ ). For monatomic ions, the charge can be thought of as a given, although other approaches treat a particle's charge as variable,<sup>4-6</sup> giving two adjustable parameters.

Helmholtz free energies of solvation,  $\Delta A_{\text{solv}}$ , were calculated using local molecular field theory (LMFT) as described previously.<sup>7</sup> These calculations include terms correcting for crossing the liquid/vapor interface, involving the surface potential, which are necessary for single ion free energies. The dependence of  $\Delta A_{\text{solv}}$  on the Lennard-Jones parameters was determined using thermodynamic integration. The thermodynamic integration used 11 equally spaced integration points with 50 ns of simulation time at each point. All simulations used the Gromacs package, with periodic boundary conditions, using particle mesh Ewald, and at constant temperature, volume, and particle number.<sup>8</sup> The Helmholtz free energies resulting from the TVN simulations are directly comparable to the experiment Gibbs free energy change,  $\Delta G_{\text{solv}}$ , because the volume change upon the addition of an ion makes a negligible contribution to the free energy. The simulations used 215 EC molecules and one ion. Parameters for EC were taken from the Amber GAFF force field.<sup>9</sup> Parameters for the ions were taken for Horinek, *et al.*, which were optimized for aqueous solutions.<sup>10</sup>

### 3. Results

The free energy results for the original and optimized parameters are given in Table 1, along with the experimental values.<sup>2</sup> The Horinek, *et al.*, parameters<sup>10</sup> underestimate the free energy. For iodide, the results are underestimated by almost 20 kcal/mol. The results for potassium are closer to experiment, but still underestimated. Determining single ion free energies, either from experiment or simulation, requires making extra-thermodynamic assumptions because it is not possible to determine the solvation energy for single ions. But for neutral ion pairs, for which no assumptions are necessary, the solvation free energies are also underestimated. By decreasing the  $\sigma$  parameter, and decreasing the separation between the ion and the solvent, the free energy can be brought into agreement with experiment (Table 1).

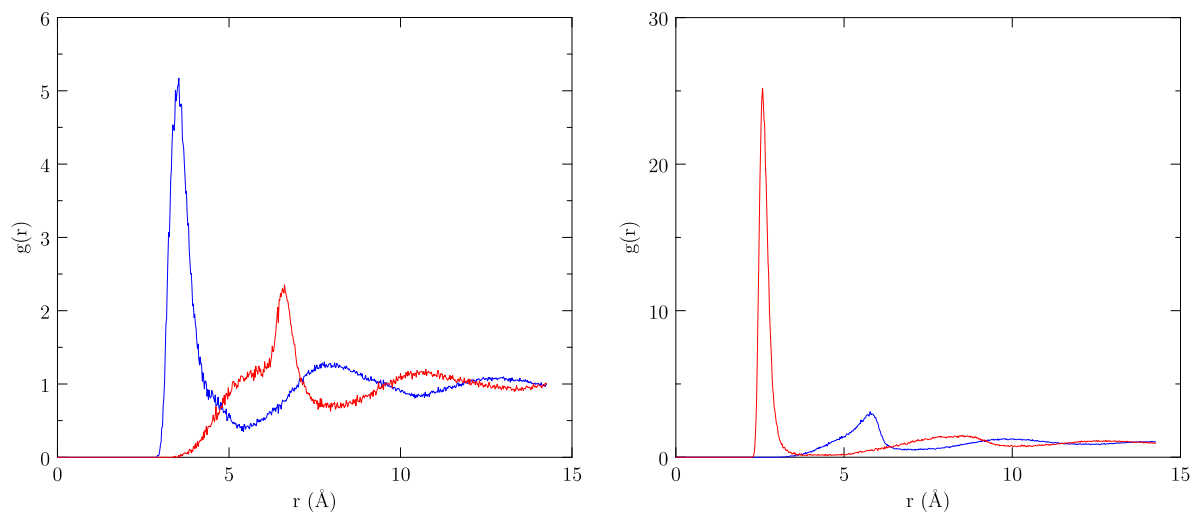
Of the ions, the potassium cation has the most negative free energy, despite have a larger ionic radius than some of the anions. In water,  $K^+$  has about the same solvation free energy as  $Cl^-$  and a significantly smaller value than the smaller  $F^-$  ion.<sup>11</sup> The EC solvent seems to show more of a preference for cations over anions than water. Weaker anion-EC interactions are also suggested by the trends in  $\Delta G_{\text{solv}}$  among the halides, which after a big

change from F<sup>-</sup> to Cl<sup>-</sup>, does not change much for Br<sup>-</sup> and I<sup>-</sup>. For water, there is a steady decrease in  $\Delta G_{\text{solv}}$  in the halide series. The anions versus cations preference was checked by calculating  $\Delta A_{\text{solv}}$  for an anion with the same Lennard-Jones parameters as sodium ( $\epsilon=0.368$  kcal/mol and  $\sigma=2.65\text{\AA}$ ). This was done using thermodynamic integration, using F<sup>-</sup>, with the original parameters, as a reference. The resulting  $\Delta A_{\text{solv}}$  for this ion was -80.4 kcal/mol, which is 8 kcal/mol less than the positively charged ion with the same Lennard-Jones parameters.

**Table 1.** Calculated free energies for different ion Lennard-Jones parameters.

ion	Horinek, <i>et al</i> parameters			EC optimized parameters			experiment
	$\epsilon$ (kcal/mol)	$\sigma$ ( $\text{\AA}$ )	$\Delta A$ (kcal/mol)	$\epsilon$ (kcal/mol)	$\sigma$ ( $\text{\AA}$ )	$\Delta A$ (kcal/mol)	$\Delta G$ (kcal/mol)
F <sup>-</sup>	0.112	3.43	-70.28	0.112	2.40	-84.6	-84.61
Cl <sup>-</sup>	0.099	4.39	-55.39	0.099	3.31	-68.6	-68.60
Br <sup>-</sup>	0.050	4.83	-53.97	0.050	3.91	-64.6	-64.77
I <sup>-</sup>	0.038	5.33	-47.21	0.038	3.55	-66.7	-66.68
K <sup>+</sup>	0.368	2.78	-85.85	0.368	2.65	-88.7	-88.67

The structure around the ion is characterized by the pair correlation function. Figure 2 shows the pair correlation functions around the Cl<sup>-</sup> and K<sup>+</sup> ions. There is a high nearest neighbor peak between K<sup>+</sup> and the O1 EC atom (see Figure 1). The nearest neighbor peak around Cl<sup>-</sup> is not as high, indicating weaker association.



**Figure 2.** Pair correlation functions between Cl<sup>-</sup> (left) and K<sup>+</sup> (right) with the C2 carbon atom (blue) and O1 oxygen atom (red) of the EC molecule.

From the pair correlation functions, coordination numbers can be determined. The  $\text{Cl}^-$  ion has 6 C2 nearest neighbors, which since there are two per molecule, corresponds to three EC neighbors. The  $\text{K}^+$  has about seven nearest neighbors.

#### 4. Conclusion

With adjustment of the Lennard-Jones parameters, solvation free energies for ions in EC can be made to agree well with experiment data. Further studies will determine other Lennard-Jones parameter pairs ( $\epsilon$  and  $\sigma$ ) that agree. Among those values, the optimal values can be chosen using additional data such as the enthalpy and entropy of solvation. The solvent displays a stronger affinity for cations over anions, as seen by the free energy data, as well as the solvation structure, in which the  $\text{K}^+$  ions has more nearest neighbors than  $\text{Cl}^-$ . This can be understood from the structure of the EC molecule, in which the negatively charged oxygen atoms, particularly O1, are well positioned to interaction with a cation. The compensating positive charge is contained in one atom, C1, which is surrounded by negatively charged oxygen atoms, so not that available for anion, or spread out among the remaining 2 carbon and 4 hydrogen atoms, so not that large (Figure 1).

#### 5. Acknowledgments

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#### 6. References

- [1] Jones, J., Anouti, M., Caillon-Caravanier, M., Willmann, P. & Lemordant, D. Lithium fluoride dissolution equilibria in cyclic alkylcarbonates and water. *J. Mol. Liq.* **153**, 146–152 (2010).
- [2] Peruzzi, N., Ninham, B. W., Nostro, P. & Baglioni, P. Hofmeister Phenomena in Nonaqueous Media: The Solubility of Electrolytes in Ethylene Carbonate. *J Phys Chem B* **116**, 14398–14405 (2012).
- [3] You, X. *et al.* Interfaces of propylene carbonate. *J Chem Phys* **138**, 114708 (2013).
- [4] **Youngs, T. G. A. & Hardacre, C. Application of static charge transfer within an ionic-liquid force field and its effect on structure and dynamics. *ChemPhysChem* **9**, 1548–1558 (2008).**
- [5] **Leontyev, I. & Stuchebrukhov, A. Accounting for electronic polarization in non-polarizable force fields. *Phys Chem Chem Phys* **13**, 2613 (2011).**
- [6] Soniat, M. & Rick, S. W. The effects of charge transfer on the aqueous solvation of ions. *J Chem Phys* **137**, 044511 (2012).
- [7] Beck, T. L. Hydration Free Energies by Energetic Partitioning of the Potential Distribution Theorem. *J. Stat. Phys.* **145**, 335–354 (2011).
- [8] Hess, B., Kutzner, C., Van Der Spoel, D. & Lindahl, E. GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comput.* **7**, 306 (2008).
- [9] Wang, J., Wang, W., Kollman, P. A. & Case, D. A. Automatic atom type and bond type perception in molecular mechanical calculations. *J. Molec. Graphics and Design* **25**, 247260 (2006).
- [10] Horinek, D. *et al.* Specific ion adsorption at the air/water interface: The role of hydrophobic solvation. *Chemical Physics Letters* **479**, 173–183 (2009).
- [11] Tissandier, M. D., Cowen, K. A. & Feng, W. Y. The proton's absolute aqueous enthalpy and Gibbs free energy of solvation from cluster-ion solvation data. *J. Phys. Chem. A* **102**, 7787–7794 (1998).