

Specific Ion Solvation in Ethylene Carbonate and Propylene Carbonate

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Outline

1. Introduction
2. Force fields
3. Energies
4. Classical structure
5. Thermodynamics
6. Cavity potentials
7. Quantum studies

EC and PC

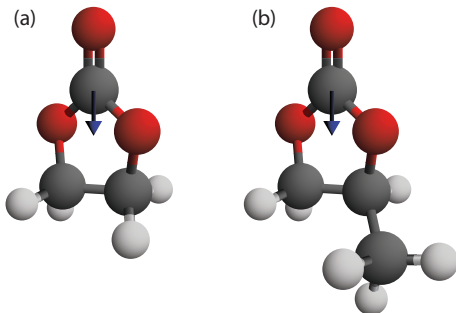


Figure: Images of the EC (a) and PC (b) molecules. Modeled with AMBER-GAFF force field. LJ and Buckingham models for ions. Fixed charges, enhanced molecular dipoles relative to gas phase. Cations bind on top (hard), anions on bottom (soft).

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EC and PC

- EC: dipole 4.61 D, ϵ 89.8, BP 515 K, MP 36.4 K, α 6.8 \AA^3
- PC: dipole 4.81 D, ϵ 64.9, BP 515 K, MP -49 K, α 8.7 \AA^3
- EC AMBER GAFF dipole 6.2 D
- PC AMBER GAFF dipole 6.4 D
- AMBER GAFF good for density, ϵ , surf tension, not so good for enthalpy of vaporization (20 % too large)
- 20 % charge reduction fixes above error, but other consequences?
- Water polarizability is only α 1.47 \AA^3

Force field and QM interactions: Li^+/EC

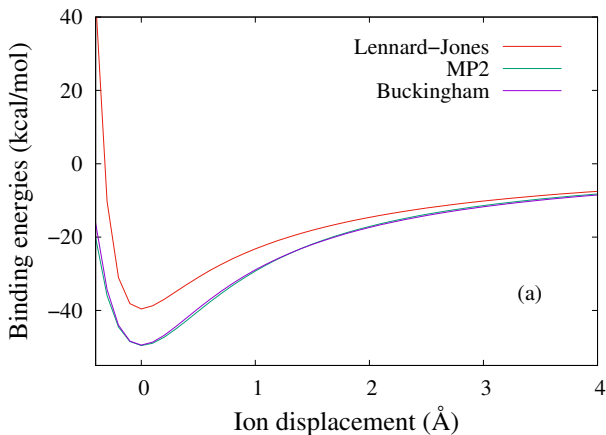


Figure: Li^+/EC (a) binding energy curves with Lennard-Jones and modified Buckingham potentials, and MP2 calculations.

Force field and QM interactions: Cl^-/EC

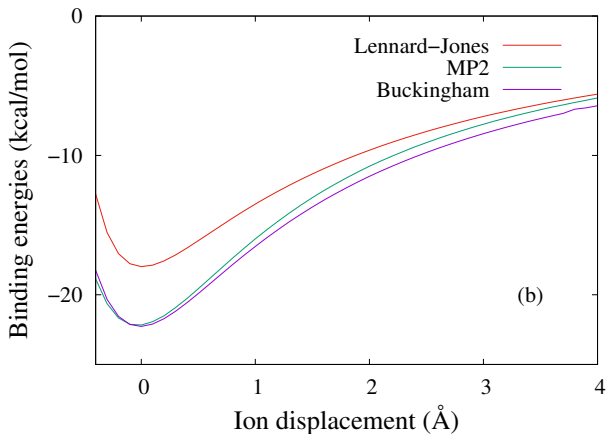


Figure: Cl^- -EC (b) binding energy curves with Lennard-Jones and modified Buckingham potentials, and MP2 calculations.

MD simulations and FE calcs

- AMBER GAFF FF for EC and PC
- LJ models taken from Horinek et al. params for ion-water
- Derived modified Buckingham model from MP2 calcs above
- PBC and Ewald
- Free energies using our LMFT-type approach; separates electrostatics into local and far field contributions
- Experimental thermodynamic data from Pierandrea Lo Nostro group's papers cited in our paper. Ion pair solubility measurements.

SAPT energy partitioning

Table: SAPT2/aug-cc-phwCVDZ interaction energies for ion-solvent dimers; all energies are given in kcal/mol.

Solvent	Ion	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{SAPT}	E_{MP2}
EC	Li ⁺	-41.63	13.55	-21.52	-0.57	-50.17	-49.57
	K ⁺	-28.04	10.08	-8.43	-1.73	-28.12	-27.42
	F ⁻	-40.83	30.97	-17.05	-5.25	-32.17	-30.62
	Cl ⁻	-28.23	19.02	-8.21	-5.43	-22.85	-22.12
	Br ⁻	-26.43	18.05	-7.01	-5.57	-20.97	-20.24
PC	Li ⁺	-43.50	13.81	-21.09	-0.50	-51.27	-51.20
	K ⁺	-29.01	10.41	-8.78	-1.77	-29.14	-28.45
	F ⁻	-39.81	31.70	-19.03	-5.79	-32.93	-30.84
	Cl ⁻	-26.90	19.27	-9.20	-6.02	-22.85	-21.82
	Br ⁻	-25.08	18.31	-7.85	-6.21	-20.84	-19.88

Ion specificity

Dispersion differs between cations and anions as expected, but weak contribution to ion specificity between anions. Electrostatics, exchange, and induction make larger contributions.

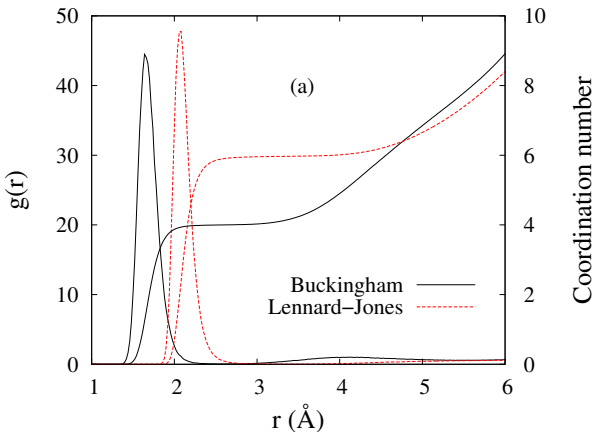
RDF Li^+/EC 

Figure: RDFs

Experiment/Theory

Experiment (neutron, Xray absorption) suggest coordination of 4-4.5. Ab initio simulation puts first maximum at about 2 Å, and 4-coordinated (see below).

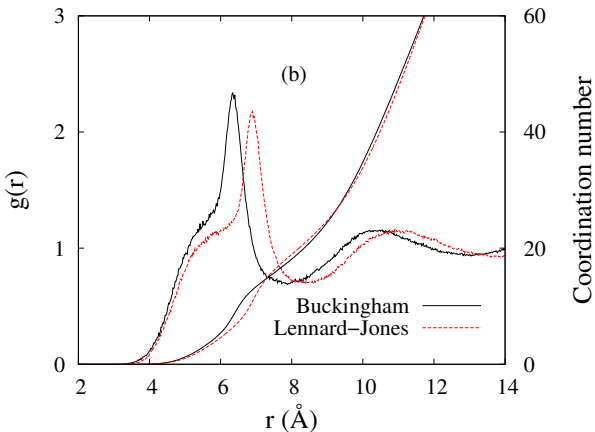
RDF Cl^-/EC 

Figure: RDFs

Ion FEs

Table: Single-ion free energies and enthalpies are calculated for the two models at $T = 313\text{ K}$ for EC and PC. U_{SR} is solvent reorganization energy. Marcus values for K^+ and Cl^- in PC are -73.2 and -76.7.

Solvent	Ion	μ_{LJ}^{ex}	h_{LJ}^{ex}	μ_{Buck}^{ex}	h_{Buck}^{ex}	s_{Buck}^{ex}	U_{SR}
EC	K^+	-84.0	-93.7	-87.8	-97.6	-31.3	60.8
	F^-	-67.0	-77.7	-82.4	-90.3	-25.2	45.2
	Cl^-	-57.8	-71.2	-68.2	-75.4	-23.0	41.9
	Br^-	-50.5	-65.8	-61.1	-70.3	-29.4	38.8
PC	K^+	-87.1	-100.9	-87.9	-99.1	-35.8	58.0
	F^-	-64.0	-77.1	-83.5	-91.9	-26.8	45.1
	Cl^-	-51.3	-65.5	-63.7	-71.6	-25.2	41.0
	Br^-	-47.1	-63.6	-59.5	-70.9	-36.4	39.6

Model comparison

Table: Free energy, enthalpy, and entropy changes of solvation. First 3 rows for EC, second 3 for PC. Potassium salts with F^- , Cl^- , Br^- . Second row adds U_{SR} correction for induced dipoles.

μ_{LJ}^{ex}	h_{LJ}^{ex}	s_{LJ}^{ex}	μ_{Buck}^{ex}	h_{Buck}^{ex}	s_{Buck}^{ex}	μ_{exp}^{ex}	h_{exp}^{ex}	s_{exp}^{ex}
-151.8(19.8)	-172.1(-3.6)	-64.9(-74.8)	-170.4(1.2)	-187.9(-19.4)	-55.9(-65.8)	-171.6	-168.5	9.9
				-179.4(-10.9)	-28.8(-38.7)			
-143.2(5.2)	-166.3(-16.6)	-73.8(-69.6)	-156.4(-8.0)	-173.3(-23.6)	-54.0(-49.8)	-148.4	-149.7	-4.2
				-164.8(-15.1)	-26.8(-22.6)			
-135.9(7.1)	-160.9(-11.0)	-79.9(-57.9)	-150.1(-7.1)	-169.1(-19.2)	-60.7(-38.7)	-143.0	-149.9	-22.0
				-160.6(-10.7)	-33.5(-11.5)			
-151.7	-178.3	-85.0	-171.4	-190.8	-62.0			
				-182.3	-34.8			
-140.4(3.6)	-168.7(-3.7)	-90.4(-24.6)	-152.4(-8.4)	-173.2(-8.2)	-66.5(0.7)	-144.4	-165.0	-65.8
				-164.7(0.3)	-39.3(26.5)			
-136.0(4.6)	-166.3(-5.4)	-96.8(-31.9)	-148.0(-7.4)	-171.1(-10.2)	-73.8(-8.9)	-140.6	-160.9	-64.9
				-162.6(-1.7)	-46.7(18.2)			

Solvent reorganization energy effect?

U_{SR} shows up in both enthalpy and entropy, but cancels in free energy. Seems like an extra repulsive contribution helps some compared with experiment. Where does this come from? We proposed it is repulsive interaction of induced dipoles (all pointing towards ion) in first solvation shell (see below).

Cycle

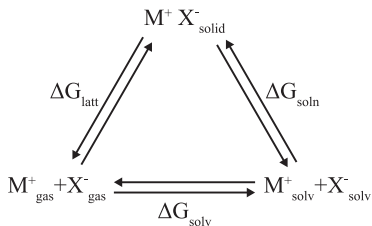


Figure: Thermodynamic cycle shows the relationship between the free energies of solution and solvation and the lattice free energy.

Volcano plot

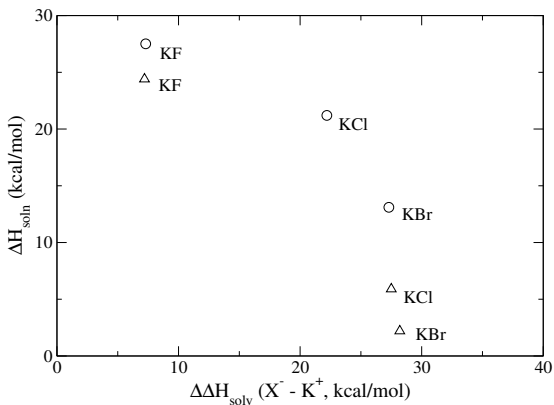
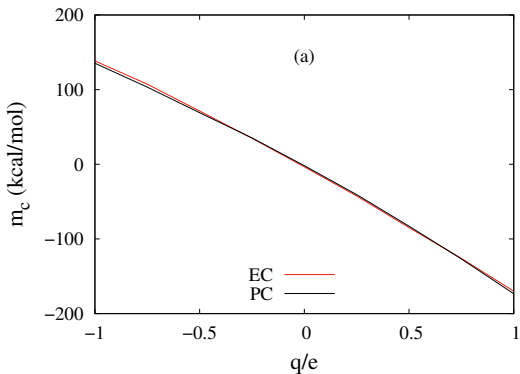


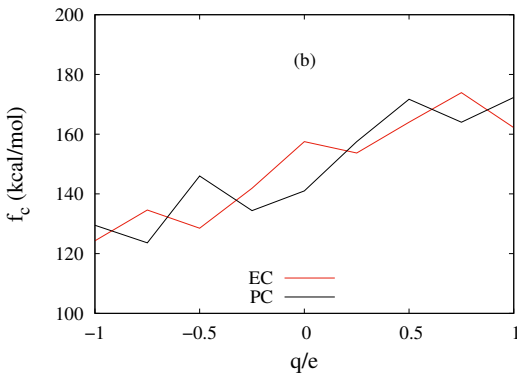
Figure: Relationship between the enthalpy of solution and the difference between the single solvation enthalpies of K^+ and halide ions (F^- , Cl^- , and Br^-) for both EC (circles) and PC (triangles). ΔH_{solv} is our calculated value.

ES mean potl at ion center vs. chg



ES potl fluct vs. chg

Quite different from water. Cations are more strongly solvated, and smooth transition as charge mutated. (Hummer, Pratt, Garcia, 1996)



ES potl vs. cavity radius

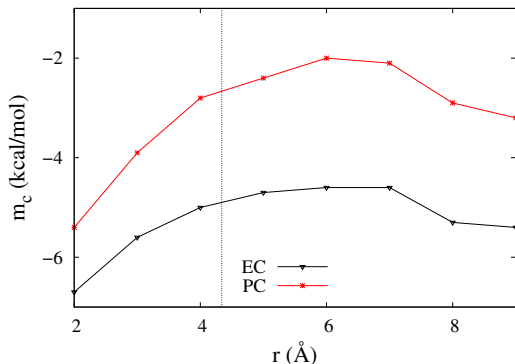
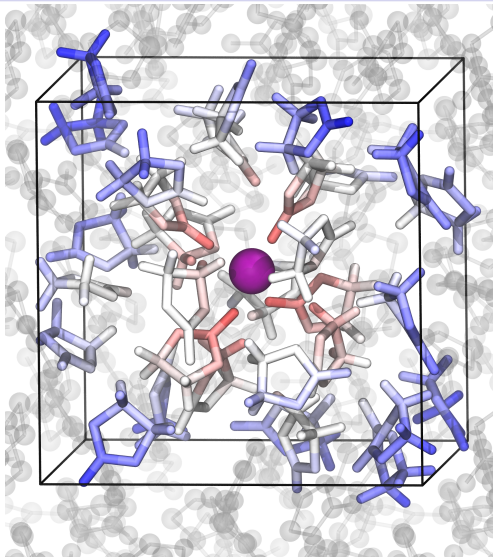
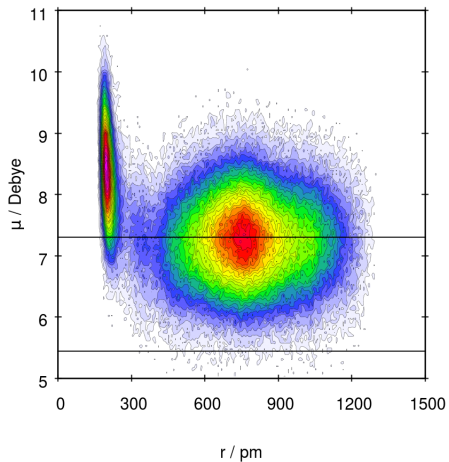


Figure: Electrostatic potential at the center of a vdW particle cavity in EC and PC as a function of the cavity radius. The dashed line shows the size of the particle (Cl^- size).

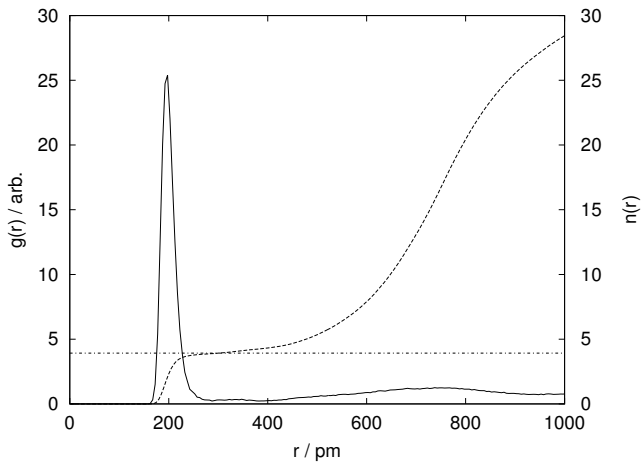
Li^+ in EC; AIMD; PBE/D3BJ; 240 ps, 31 EC



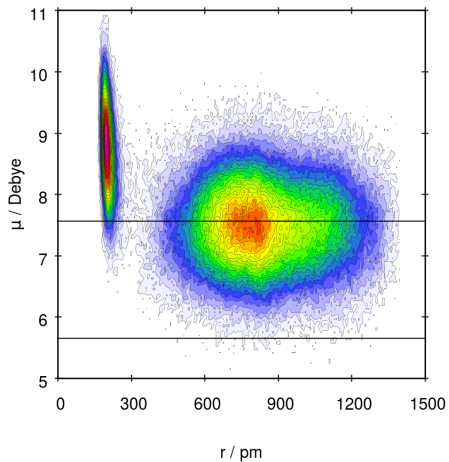
EC dipoles near and far from Li^+



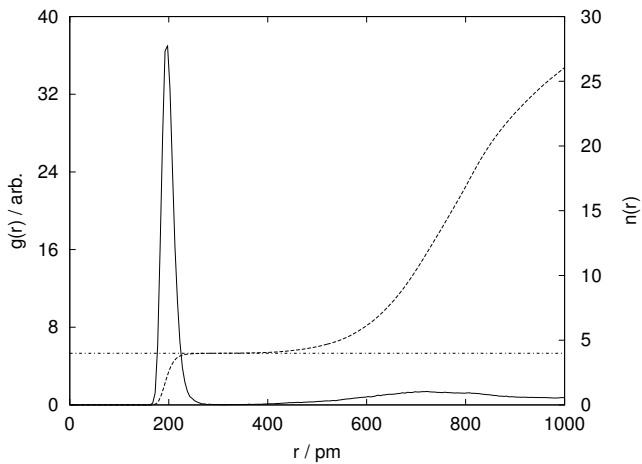
$g(r)$ for Li^+/EC



PC dipoles near and far from Li^+



$g(r)$ for Li^+/PC



Conclusions

- Classical models can yield some insights into solvation
- But they struggle to reproduce solvation thermodynamic quantities
- Fixed charges can to some extent mimic polarization in pure solvent condensed phase, but can't reproduce ion solvation quantities
- Polarization is extreme near Li^+ ion – that is likely important for solvation thermodynamics in EC especially – it tends to disorder the solvation shell and creates repulsive solvent-solvent interactions