Supplementary Information: Interfacial Structure and Structural Forces in Mixtures of Ionic Liquid with a Polar Solvent

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I. FORCE FIELD INFORMATION

This section describes the forcefields used in the molecular dynamics simulations described in this paper. These forcefields are based on the OPLS-AA forcefield[1] with additional reparamaterisation having been performed in previous work[2–5].

The atoms within the forcefield are denoted as shown in Fig. S1. Additionally to this hydrogen atoms bonded to the ring carbons in the cation are defined as cHr, while the hydrogen atoms bonded to tail atoms are defined as cHt.

A. Non-bonded Parameters

Below are the non-bonded parameters, due to the different value of ε_r, the partial charges on propylene carbonate molecule are scaled up.

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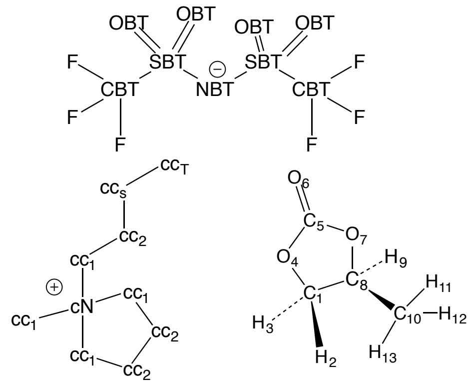

FIG. S1. *A cartoon showing the assignment of atom names within the forcefield.*

Atom Name	Mass	charge (e)	σ (nm)	ε (kJ mol^{-1})
NBT	14.000	-0.66	0.325	7.113×10^{-1}
OBT	15.999	-0.53	0.295	8.786×10^{-1}
CBT	12.011	0.35	0.350	2.761×10^{-1}
SBT	32.066	1.02	0.355	1.0462
F	18.998	-0.16	0.295	2.218×10^{-1}
cN	14.000	0.12	0.325	7.113×10^{-1}
cC_1	12.011	-0.17	0.350	2.761×10^{-1}
cC_2	12.011	0.13	0.350	2.761×10^{-1}
cC_T	12.011	-0.18	0.350	2.761×10^{-1}
cC_S	12.011	-0.12	0.350	2.761×10^{-1}
cHr	1.008	0.13	0.25	1.255×10^{-1}
cHt	1.008	0.06	0.25	1.255×10^{-1}
C_1	12.011	0.12	0.355	2.761×10^{-1}
H_2	1.008	0.09875	0.242	6.276×10^{-2}
H_3	1.008	0.1	0.242	6.276×10^{-2}
O_4	15.999	-0.5075	0.300	7.113×10^{-1}
C_5	12.011	1.060125	0.375	4.393×10^{-1}
O_6	15.999	-0.69025	0.296	8.786×10^{-1}
O_7	15.999	-0.50825	0.300	7.113×10^{-1}
C_8	12.011	0.139875	0.355	2.761×10^{-1}
H_9	1.008	0.1075	0.242	6.276×10^{-2}
C_{10}	12.011	-0.138875	0.355	2.761×10^{-1}
H_{11}	1.008	0.071	0.242	6.276×10^{-2}
H_{12}	1.008	0.06525	0.242	6.276×10^{-2}
H_{13}	1.008	0.082375	0.242	6.276×10^{-2}

For the electrode atoms σ is set as 0.355 nm and ε as 0.29288 KJmol^{-1}. Standard OPLS-AA combination rules are used to generate potentials for unlike atoms.

B. Bonded Parameters

A large number of atom types have the same bonded parameters, within the cation all carbon atoms are treated as a single type cC, and all hydrogen atoms as cH. While in propylene carbonate molecule all hydrogen atoms are defined as H, all carbon atoms except for the carbonyl, C_5, defined as C_T, and the non carbonyl oxygens defined as OS.

C. Bonds

Bonds are modelled using a harmonic potential defined below,

$$V_{\text{bond}}(r_{ij}) = \frac{1}{2}k^b_{ij}(r_{ij} - b_{ij})^2, \tag{1}$$

where b_{ij} is the equilibrium bond length, k^b_{ij} is the force constant, and r_{ij} is the separation between two atoms. The values of these constants are shown below.

i	j	b_{ij} (nm)	k^b_{ij}(kJ mol^{-1}nm^{-2})
NBT	SBT	0.1570	3.137×10^5
SBT	OBT	0.1437	5.331×10^5
SBT	CBT	0.1818	1.950×10^5
CBT	F	0.1323	3.698×10^5
cN	cC	0.1471	3.071×10^5
cC	cC	0.1529	2.242×10^5
cC	cH	0.1090	2.845×10^5
C_T	C_T	0.1529	2.242×10^5
C_T	OS	0.1410	2.678×10^5
C_5	O_6	0.1229	4.769×10^5
C_5	OS	0.1327	1.791×10^5
C_T	H	0.1090	2.845×10^5

D. Angles

Angles are modelled using a harmonic potential defined below,

$$V_{\text{angle}}(\theta_{ijk}) = \frac{1}{2}k^\theta_{ijk}(\theta_{ijk} - \theta^0_{ijk})^2, \tag{2}$$

where θ^0_{ijk} is the equilibrium angle, k^θ_{ijk} is the force constant, and ${k^\theta_{ijk}}^0$ is the separation between two atoms. The values of these constants are shown below.

i	j	k	θ^0_{ijk} (degrees)	k^θ_{ijk} (kJ mol^{-1} rad^{-2})
NBT	SBT	OBT	113.6	789.0
NBT	SBT	CBT	103.5	764.0
SBT	CBT	F	111.7	694.0
SBT	NBT	SBT	125.6	671.0
CBT	SBT	OBT	102.6	870.0
OBT	SBT	OBT	118.5	969.0
F	CBT	F	107.1	781.0
cN	cC	cC	109.5	669.4
cN	cC	cH	109.5	209.2
cC	cN	cC	109.5	418.4
cC	cC	cC	112.7	488.3
cC	cC	cH	110.7	313.8
cH	cC	cH	107.8	276.1
O_6	C_5	OS	123.4	694.5
C_5	OS	C_T	116.9	694.5
OS	C_T	H	109.5	292.9
C_T	C_T	C_T	112.7	488.3
C_T	C_T	H	110.7	313.8
H	C_T	H	107.8	276.1
C_T	C_T	OS	109.5	418.4

1. Dihedrals

The dihedral interactions are modelled using the Ryckaert-Bellemans formulation (which is related to the standard OPLS dihedral formulation),

$$V_{\text{dihedral}}(\phi_{ijkl}) = \sum_{n=0}^{5} C_n(\cos(\phi_{ijkl}))^n, \tag{3}$$

Where C_n is the coefficient for term n in the sum. The values of C_n for numbers 0 to 3 are shown below. For all dihedral interactions the values of C_4 and C_5 are equal to 0 kJ mol^{-1}.

i	j	k	l	C_0 (kJ mol^{-1})	C_1 (kJ mol^{-1})	C_2 (kJ mol^{-1})	C_3 (KJmol^{-1})
NBT	SBT	CBT	F	0.661	1.983	0.000	-2.644
SBT	NBT	SBT	OBT	-0.008	-0.023	0.000	0.030
SBT	NBT	SBT	CBT	4.369	-21.179	10.420	6.390
OBT	SBT	CBT	F	0.726	2.177	0.000	-2.902
cN	cC	cC	H	-4.0962	-1.552	2.967	-3.958
cN	cC	cC	cC	6.975	0.000	-0.820	-4.602
cC	cN	cC	cC	1.771	3.516	0.536	-5.816
cC	cN	cC	H	1.715	5.088	0.000	-4.686
cC	cC	cC	cC	2.929	-1.464	0.209	-1.674
cH	cC	cC	cH	0.726	2.177	0.000	-2.902
cH	cC	cC	cC	0.726	2.177	0.000	-2.902
H	C_T	C_T	H	0.628	1.883	0.000	-2.510
H	C_T	C_T	C_T	0.628	1.883	0.000	-2.510
O_6	C_5	OS	C_T	20.920	0.000	-20.920	0.000
C_5	OS	C_T	C_T	-2.197	5.201	0.527	-3.531
C_5	OS	C_T	H	0.414	1.243	0.000	-1.657
OS	C_T	C_T	C_T	2.874	0.582	2.092	-5.548
OS	C_T	C_T	H	0.979	2.937	-3.916	-2.902

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