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Supporting Information

for

Monte Carlo Simulation and SAFT Modeling Study of the Solvation Thermodynamics of Dimethylformamide, Dimethylsulfoxide, Ethanol and 1-Propanol in the Ionic Liquid Trimethylbutylammonium Bis(trifluoromethylsulfonyl)imide

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S1. TRANSFERABLE POTENTIALS

The equation for the classical AMBER/OPLS style force field used here is as follows

$$U_{\text{tot}} = U_{\text{ext}} + U_{\text{int}}$$

$$U_{\text{ext}} = U_{\text{disp(vdW)}} + U_{\text{rep}} + U_{\text{pol}} + U_{\text{el}}$$

$$U_{\text{int}} = U_{\text{str}} + U_{\text{bend}} + U_{\text{tors}} + U_{\text{improper}} \qquad \backslash*$$

$$U_{\text{tot}} = \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N} 4\varepsilon_{ij}\left[\left(\frac{\sigma}{r}\right)_{ij}^{12} - \left(\frac{\sigma}{r}\right)_{ij}^{6}\right]}_{U_{\text{disp(vdW)}}+U_{\text{rep}}} + \underbrace{\sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{q_i q_j}{r_{ij}}}_{U_{\text{el}}} +$$

$$\underbrace{\sum_{\text{bonds}} K_r\left(r-r_0\right)^2}_{U_{\text{str}}} + \underbrace{\sum_{\text{angles}} K_\theta\left(\theta-\theta_0\right)^2}_{U_{\text{bend}}} + \underbrace{\sum_{\text{dihed}} K_\chi\left[1+\cos\left(n\chi-\delta\right)\right]}_{U_{\text{tors}}}$$

MERGEFORMAT (1)

where U_{ext} stands for external (intermolecular) energy between distinct molecules and U_{int} is the intramolecular energy between sites belonging to the same molecule, $U_{\text{disp(vdW)}}$ is the van der Waals dispersion energy, U_{rep} is the repulsive energy, U_{pol} is the polarization energy, U_{el} is the electrostatic potential energy, U_{str} is the stretching energy associated with the variation of bond length, U_{bend} is the bending energy arising from the angular fluctuations formed by two adjacent chemical bonds, U_{tors} is the torsion energy caused by the variation of the dihedral angles formed by four successive sites in a chain, U_{improper} is the improper torsion energy pertains to the energy that enforce an aromatic ring or a conjugated structure to keep its planar form. The force fields used in this work are all nonpolarizable and there are no rings or conjugated structures present in the molecular architectures. Therefore, U_{pol} and U_{improper} are omitted from eq *

MERGEFORMAT (1). The constituent terms of the extended equations are: K_r, K_θ, and K_χ which are energy coefficients for bonds, angles, and dihedrals contributions, respectively, ε_{ij} and σ_{ij} are the energy and size parameters between sites i and j in the Lennard-Jones (LJ) potential, and q_i is the charge placed on the center of site i. Also, Lorentz-Berthelot[1, 2] combining rules were the basis for calculating of the mixed site-site interactions.

For the [Tf_2N] anion, like Zhong et al.[3] and Liu et al.[4] a scaling factor of ½ has been used for both of the Coulombic and LJ interactions between molecular sites separated by three consecutive bonds. However, this factor set to zero for sites separated by less than three consecutive bonds. The bond, angle, and dihedral terms are taken from Zhong and coworkers[3] and their values have been listed in Tables S1 of this Supporting Information. The LJ parameters for the cation, however, were modified from the work of Zhong et al.[3] as discussed in subsequent sections. The [N_{1114}] cation is based on the TraPPE-UA force field for alkanes[5], amines[6] and ammonium[7] in which a scaling factor of ½ has been implemented for Coulombic and LJ interactions. In this case, there is also a need for LJ parameter optimization based on the experimental liquid density and surface tension of [N_{1114}][Tf_2N], as discussed in the next section.

For EtOH and C_3OH, bonds, angles, dihedral, and LJ terms are taken from a UAM version of TraPPE-Alcohols[6, 8] which applies a scaling factor of ½ to both the LJ and Coulombic terms. This force field has been tested against experimental vapor pressure, heat of vaporization, and liquid density data and hence there was no need for further calibration/optimization.

DMF and DMSO follow a rigid OPLS type of the force field proposed by Chalaris and Samios[9-11], and Mancera and coworkers[12]. Clearly, the 1-4 scaling parameter is set to ½ for LJ and Coulombic terms in an OPLS force field style. For DMSO, however, another Gromos type

force field based on traditional potential types for biomolecules has also been proposed and calibrated against the experimental vapor pressure and liquid density data.

Table S1. Force field parameters for the solutes and the ionic liquid considered in this work.

Non-bonded terms			
	vdW parameters	Charges (e)	
	Ethanol		
UA sites	σ / Å	ε / K	q / e
CH_3^{alk}	3.75	98.0	0.00
CH_2^{A}	3.95	46.0	0.265
O^{A}	3.02	93.0	-0.700
H^{A}	0.00	0.00	0.435
	1-Propanol		
UA sites	σ / Å	ε / K	q / e
CH_3^{alk}	3.75	98.0	0.00
CH_2^{alk}	3.95	46.0	0.000
CH_2^{A}	3.95	46.0	0.265
O^{A}	3.02	93.0	-0.700
H^{A}	0.00	0.00	0.435
	Dimethylformamide		
UA sites	σ / Å	ε / K	q / e
CH_3^{DMF}	3.80	69	0.28
N^{DMF}	3.20	144	-0.57
C^{DMF}	3.70	47.3	0.45
O^{DMF}	2.96	226	-0.50
H^{DMF}	2.20	7.18	0.06
	Dimethylsulfoxide		
UA sites	σ / Å	ε / K	q / e
CH_3^{DMSO}	3.81	125	0.160
S^{DMSO}	3.47	214	0.139
O^{DMSO}	2.83	176	-0.459
	Bis(trifluoromethylsulfonyl)imide		
UA sites	σ / Å	ε / K	q / e
O^{Tf2N}	2.96	106	-0.398
CF_3^{Tf2N}	4.47	80.5	-0.095
S^{Tf2N}	3.56	126	0.627
N^{Tf2N}	3.25	85.6	-0.272
	Trimethylbutylammonium		
UA sites	σ / Å	ε / K	q / e

CH_3^N	3.57	98.0	0.175
CH_2^N	3.75	46.0	0.175
N^{AM}	3.25	185	0.100
CH_2^{alk}	3.95	46.0	0.00
CH_3^{alk}	3.75	98.0	0.00
Bonded terms			
	Ethanol		
Bond	K_l / K Å^{-2}	l_0 / Å	
CH_3^{alk}- CH_2^A	Fixed	1.54	
CH_2^A- O^A	Fixed	1.43	
O^A-H^A	Fixed	0.945	
	1-Propanol		
	K_l / K Å^{-2}	l_0 / Å	
CH_3^{alk}- CH_2^{alk}	Fixed	1.54	
CH_2^{alk}- CH_2^A	Fixed	1.54	
CH_2^A- O^A	Fixed	1.43	
O^A-H^A	Fixed	0.945	
	Dimethylformamide		
	K_l / K Å^{-2}	l_0 / Å	
CH_3^{DMF}- N^{DMF}	Fixed	1.44	
N^{DMF}- C^{DMF}	Fixed	1.13	
C^{DMF}- O^{DMF}	Fixed	1.23	
H^{DMF}-C^{DMF}	Fixed	1.12	
	Dimethylsulfoxide		
	K_l / K Å^{-2}	l_0 / Å	
CH_3^{DMSO}- S^{DMSO}	Fixed	1.80	
S^{DMSO}- O^{DMSO}	Fixed	1.53	
	Bis(trifluoromethylsulfonyl)imide		
	K_l / K Å^{-2}	l_0 / Å	
CF_3^{Tf2N}- S^{Tf2N}	Fixed	2.40	
O^{Tf2N}- S^{Tf2N}	Fixed	1.45	
S^{Tf2N}- N^{Tf2N}	Fixed	1.57	
	Trimethylbutylammonium		
CH_3^N-N^{AM}	Fixed	1.45	
CH_2^N- N^{AM}	Fixed	1.45	
CH_2^N- CH_2^{alk}	Fixed	1.54	
CH_2^{alk}- CH_2^{alk}	Fixed	1.54	
CH_2^{alk}- CH_3^{alk}	Fixed	1.54	
Angle terms			
	Ethanol		
Angle		K_θ / K rad^{-2}	θ_0 / degrees
CH_3^{alk}- CH_2^A-O^A		25200	109.47

CH_2^A- O^A-H^A		27700	108.5	
	1-Propanol			
		K_θ / K rad^{-2}	θ_0 / degrees	
CH_3^{alk}- CH_2^{alk}- CH_2^A		31250	114	
CH_2^{alk}- CH_2^A-O^A		25200	109.47	
CH_2^A-O^A-H^A		27700	108.5	
	Dimethylformamide			
		K_θ / K rad^{-2}	θ_0 / degrees	
H^{DMF}-C^{DMF}-N^{DMF}		Fixed	114.5	
H^{DMF}-C^{DMF}-O^{DMF}		Fixed	122.5	
N^{DMF}-C^{DMF}-O^{DMF}		Fixed	123	
C^{DMF}-N^{DMF}- $CH_{3,1}^{DMF}$		Fixed	120	
C^{DMF}-N^{DMF}-$CH_{3,2}^{DMF}$		Fixed	119	
$CH_{3,1}^{DMF}$- N^{DMF}-$CH_{3,2}^{DMF}$		Fixed	121	
	Dimethylsulfoxide			
		K_θ / K rad^{-2}	θ_0 / degrees	
O^{DMSO}-S^{DMSO}-CH_3^{DMSO}		Fixed	106.75	
CH_3^{DMSO}- S^{DMSO}- CH_3^{DMSO}		Fixed	97.40	
	Bis(trifluoromethylsulfonyl)imide			
		K_θ / K rad^{-2}	θ_0 / degrees	
CF_3^{Tf2N}- S^{Tf2N}-O^{Tf2N}		38500.252	103.2	
S^{Tf2N}-N^{Tf2N}-S^{Tf2N}		30800.201	125.2	
N^{Tf2N}-S^{Tf2N}-O^{Tf2N}		35329.643	112.7	
O^{Tf2N}- S^{Tf2N}- O^{Tf2N}		37544.036	114.6	
CF_3^{Tf2N}- S^{Tf2N}-N^{Tf2N}		39708.103	105.9	
	Trimethylbutylammonium			
		K_θ / K rad^{-2}	θ_0 / degrees	
CH_3^N-N^{AM}-CH_3^N		25178	109.5	
N^{AM}-CH_2^N-CH_3^{alk}		28300	109.5	
CH_2^N-CH_2^{alk}-CH_2^{alk}		31250	114	
CH_2^{alk}-CH_2^{alk}-CH_3^{alk}		31250	114	
Torsion terms				
	Ethanol (CHARMM)			
	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}
CH_3^{alk}- CH_2^A-O^A-H^A	0	1.74	-0.243	1.56
	1-Propanol (CHARMM)			
	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}
CH_3^{alk}-CH_2^{alk}-CH_2^A-O^A	0	1.47	-0.444	6.40
CH_2^{alk}-CH_2^A-O^A-H^A	0	1.75	-0.243	1.56
	Dimethylformamide (OPLS)			
		a_0 / kJ mol^{-1}	n	δ / kJ mol^{-1}
H^{DMF}-C^{DMF}-N^{DMF}-$CH_{3,1}^{DMF}$		0	0	41.84
H^{DMF}-C^{DMF}-N^{DMF}-$CH_{3,2}^{DMF}$		1	2	41.84

O^{DMF}-C^{DMF}-N^{DMF}-$CH_{3,1}{}^{DMF}$		1	2	41.84
O^{DMF}-C^{DMF}-N^{DMF}-$CH_{3,2}{}^{DMF}$		1	2	41.84
	Dimethylsulfoxide (no dihedral)			
Bis(trifluoromethylsulfonyl)imide (mixture of OPLS & CHARMM)				
	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}
$CF_3{}^{Tf2N}$-S^{Tf2N}-N^{Tf2N}-S^{Tf2N}	0	3.83	-4.37	-1.60
		a_0 / kJ mol^{-1}	n	δ / kJ mol^{-1}
S^{Tf2N}-N^{Tf2N}-S^{Tf2N}-O^{Tf2N}		3.35	3	0
	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}
S^{Tf2N}-N^{Tf2N}-S^{Tf2N}- $CF_3{}^{Tf2N}$	0	3.83	-4.37	-1.60
Trimethylbutylammonium (mixture of OPLS & CHARMM)				
		a_0 / kJ mol^{-1}	n	δ / kJ mol^{-1}
$CH_3{}^{N}$-N^{AM}-$CH_2{}^{N}$- $CH_2{}^{alk}$		0.65	3	59.99
N^{AM}-$CH_2{}^{N}$-$CH_2{}^{alk}$-$CH_2{}^{alk}$		0.65	3	-179.99
	a_0 / kJ mol^{-1}	a_1 / kJ mol^{-1}	a_2 / kJ mol^{-1}	a_3 / kJ mol^{-1}
$CH_2{}^{N}$-$CH_2{}^{alk}$-$CH_2{}^{alk}$- $CH_3{}^{alk}$	0	2.79	-0.57	6.58

S2. TraPPE-UA RESULTS FOR ETHANOL AND 1-PROPANOL

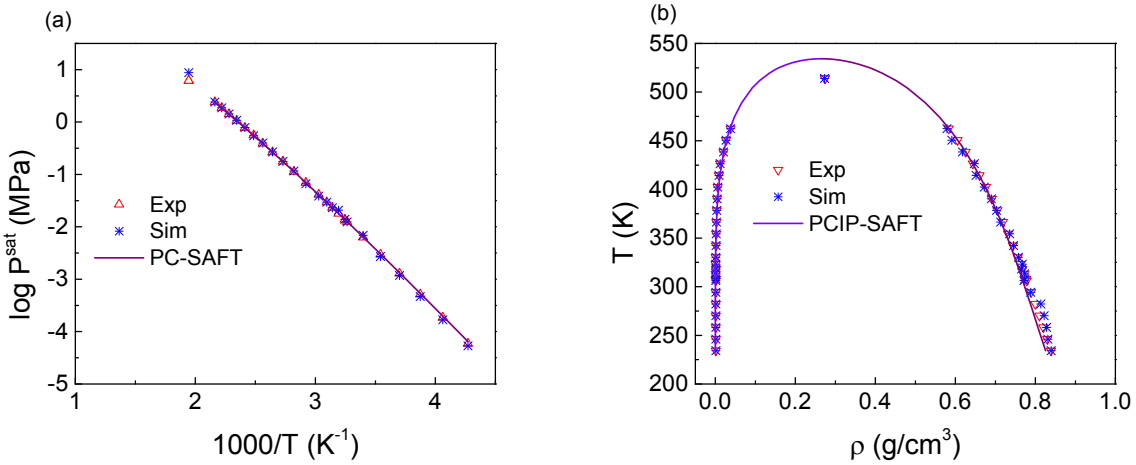

Figure S1. Vapor pressure and phase coexistence curve for ethanol based on TraPPE-UA force field.[13-15]

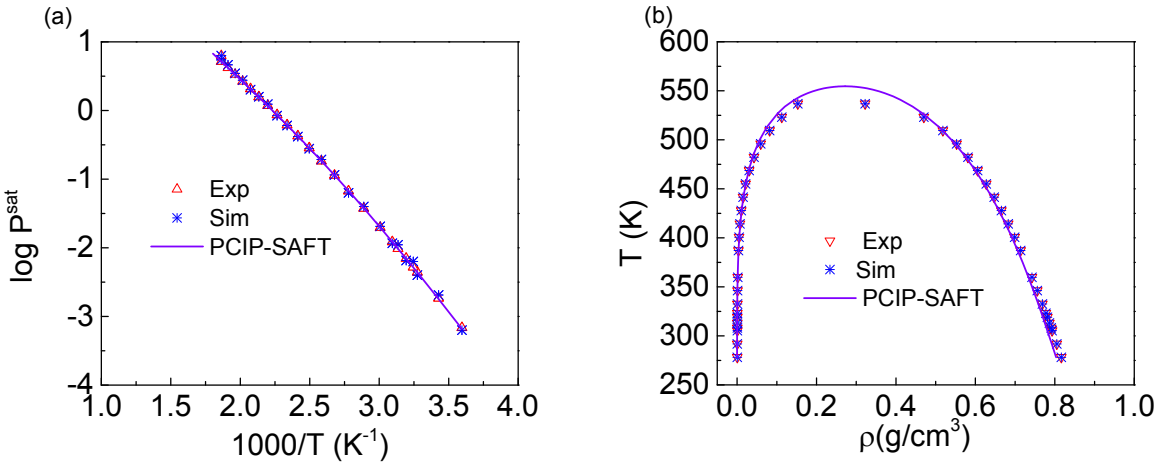

Figure S2. Vapor pressure and phase coexistence curve for 1-propanol based on TraPPE-UA force field.

S3. EXCESS AND MIXING VOLUME TRENDS

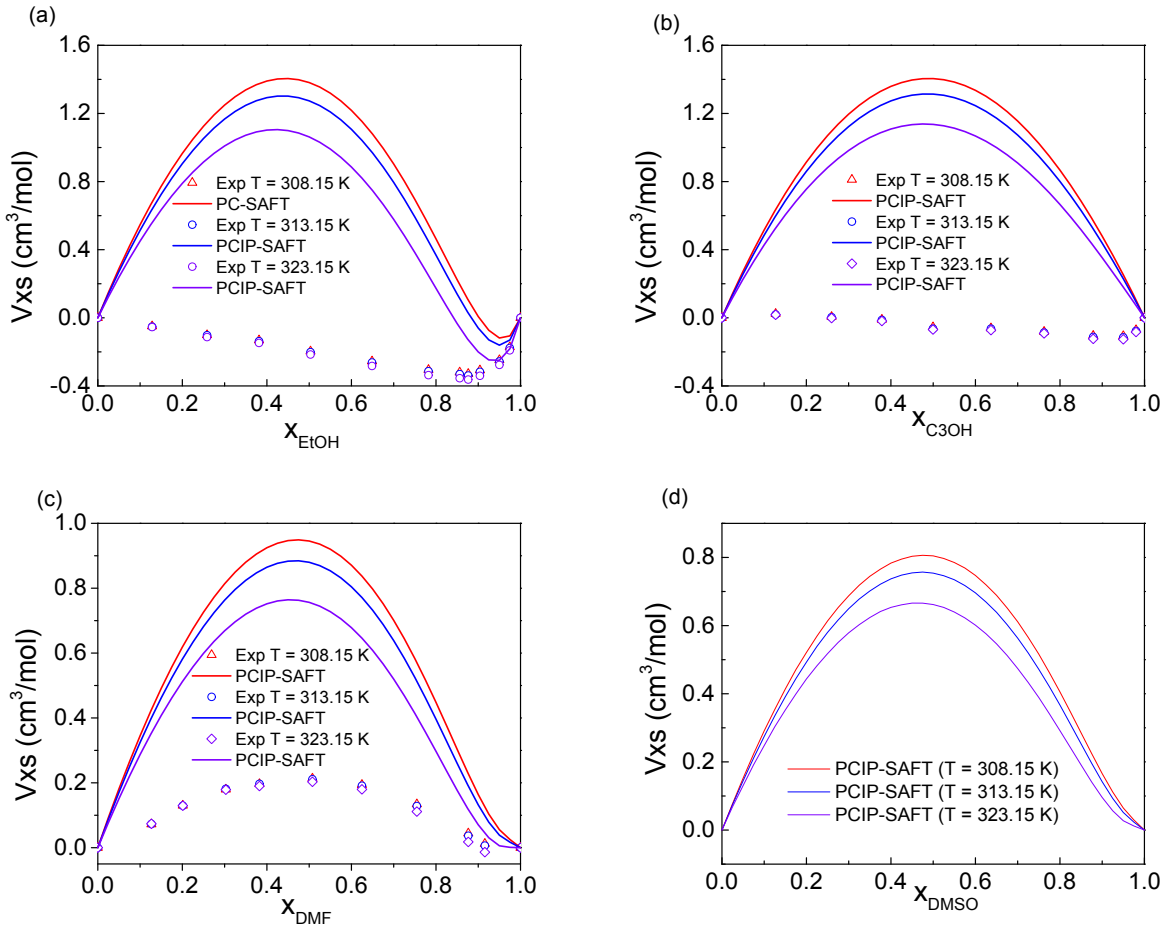

Figure S3. Trends in the excess volume of the mixing based on the experimental data and PCIP-SAFT theory for EtOH (a), C3OH (b), DMF (c), and DMSO (d). The simulation results oscillate around zero and are not shown here.

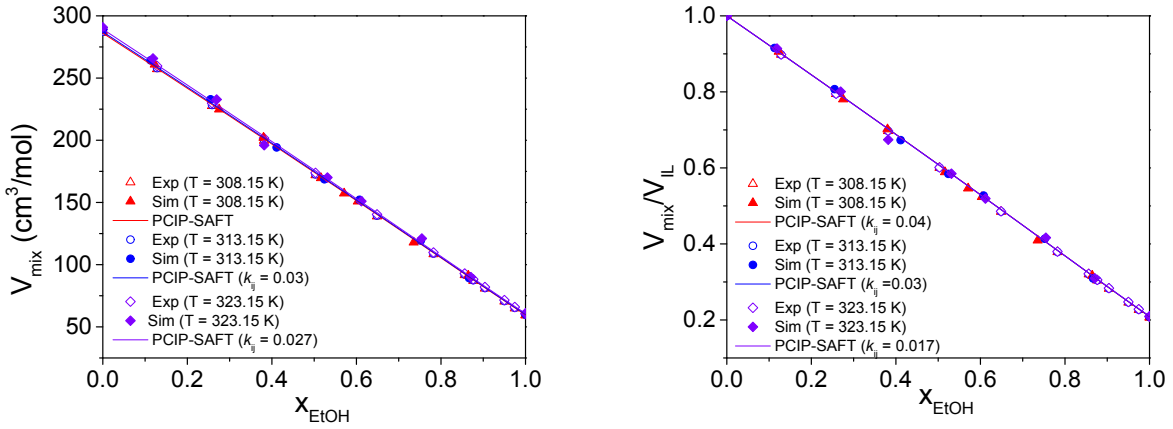

Figure S4. Comparison between experimental, simulation, and PCIP-SAFT theory for mixture molar volumes versus mole fraction of EtOH. The experimental data are taken from Massel et al.[16] The open symbols show the experimental data, the filled symbols are the MC-NPT simulation results, and the lines represent the PCIP-SAFT theory results.

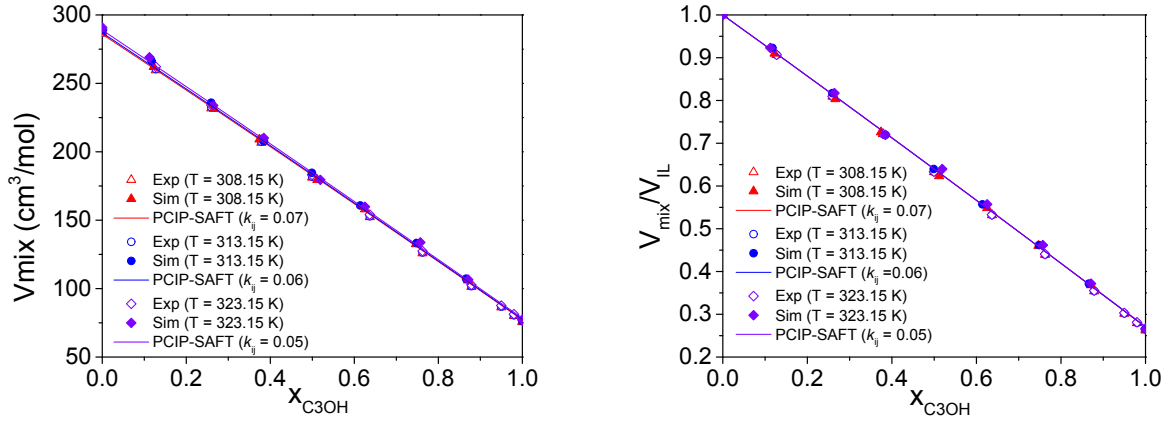

Figure S5. Comparison between experimental, simulation, and PCIP-SAFT theory for mixture molar volumes versus mole fraction of C3OH. The experimental data are taken from Massel et al.[16] The open symbols show the experimental data, the filled symbols are the MC-NPT simulation results, and the lines represent the PCIP-SAFT theory results.

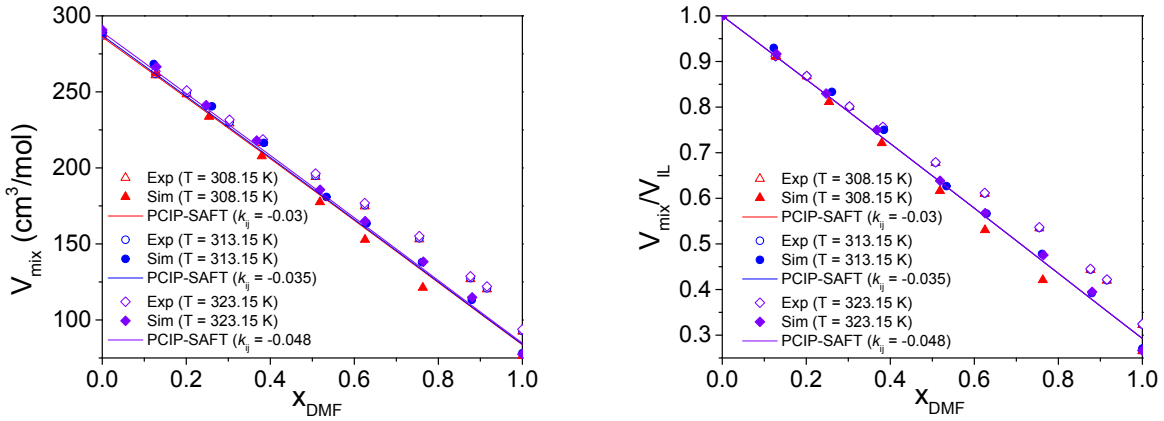

Figure S6. Comparison between experimental, simulation, and PCIP-SAFT theory for mixture molar volumes versus mole fraction of DMF. The experimental data are taken from Massel et al.[16] The open symbols show the experimental data, the filled symbols are the MC-NPT simulation results, and the lines represent the PCIP-SAFT theory results.

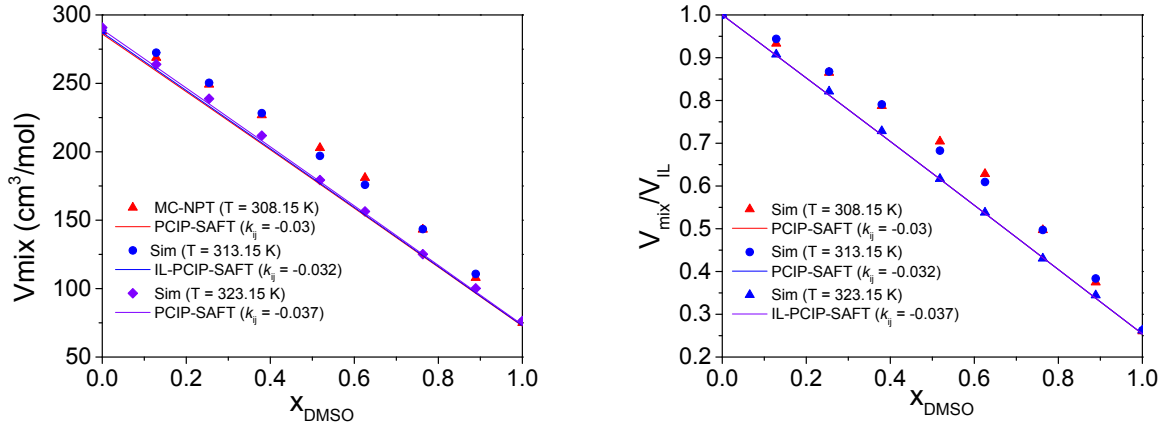

Figure S7. Comparison between experimental, simulation, and PCIP-SAFT theory for mixture molar volumes versus mole fraction of DMSO. The experimental data are taken from Massel et al.[16] The open symbols show the experimental data, the filled symbols are the MC-NPT simulation results, and the lines represent the PCIP-SAFT theory results.

S4. IONIC LIQUID SITE-SOLUTES SDF

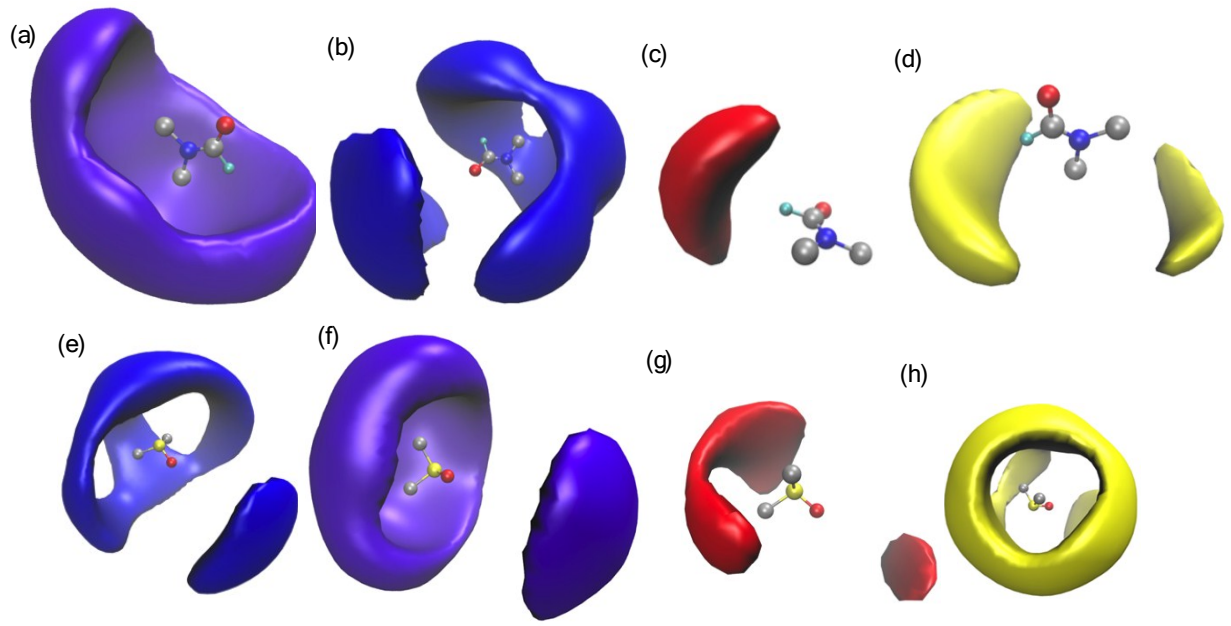

Figure S8. Spatial distribution function for (a) DMF-CF3^{Anion}, (b) DMF-N^{Anion}, (c) DMF-O^{Anion}, (d) DMF-S^{Anion}, (e) DMSO- CF3^{Anion}, (f) DMSO- N^{Anion}, (g) DMSO- O^{Anion}, (h) DMSO- S^{Anion}. The isosurface value is chosen to be 2.313 pm^{-3} at concentration of 0.5 of the solutes.

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