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Determining Physical Properties of N-alkylpyridinium Ionic Liquids Using OPLS Force Fields

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Introduction

Ionic liquids (ILs) are salts that are typically liquid at room temperature and normally consist of a large, asymmetric cation and a stable, relatively inert anion. In this case, the cations being investigated are N-alkylpyridinium ions (Figure 1), while there are three anions of interest, BF_4, DCA, and TFSI (Figure 2). ILs have recently become of great commercial interest with applications in carbon capture, batteries and cellulose processing. As a result, experiments to determine the physical properties of these substances have become more common, ostensibly to determine the optimal ionic liquid for various situations. In this same vein, force fields and force field parameters, such as the OPLS-2009IL parameters developed by other members of the lab, are constantly being refined in an attempt to accurately predict the properties of these ionic liquids. Though the lab previously tested the OPLS-2009IL parameters on a few N-alkylpyridinium based ILs, here I seek to expand the testing by using a wider array of systems and temperatures.

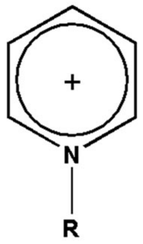
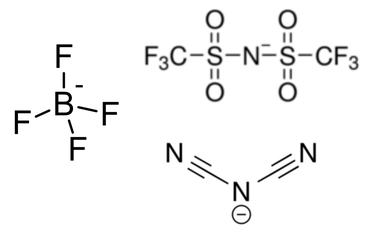


Figure 1. IL-forming N-alkylpyridinium Here, R can be ethyl [EPyr], propyl [PrPyr], butyl [BPyr], pentyl [PPyr], hexyl [HPyr], or octyl [OPyr]

Figure 2. The three anions of interest Clockwise, from left, tetrafluroborate (BF_4), bis(trifluoromethanesulfon)imide (TFSI), and dicyanamide (DCA).



Methodology

- Systems simulated using molecular dynamics in GROMACS 5.0.7
- Cubic boxes containing 500 ion pairs were generated using Packmol to run the simulations before minimizing them using a steepest descent algorithm
- Simulations performed at a range of temperatures from 278 K to 363 K.
- Systems were equilibrated at NPT for 5 ns. After that, production simulations would run for 40 ns.
- Charges were scaled by 0.8 in order to mimic polarization that would otherwise be very computationally expensive to simulate.
- Surface tension was calculated at 425 K with the Z dimension of the box tripled and extrapolating from multiple experimental values found in literature for comparison. The equation $[l_z*(P_x-P_y-2P_z)]/4$ was used to calculate the surface tension where l_z is the length in the z direction and P_x, P_y, and P_z are pressure values along the x, y and z axes, respectively.
- Viscosity required up to 10 additional runs for a length of 10 ns each. Regression-based analysis using the non-equilibrium periodic perturbation method was then used to determine viscosity values.
- The radial distribution function (RDF) was calculated using the program TRAVIS using trajectory input from GROMACS, and plotted in Excel.

Results

Table 1. Density (g/cm^3) as a Function of Temperature

Ionic Liquid	T(K)	OPLS	Experimental	% Error
[BPyr][DCA]	298	1.043	1.09006	4.3
	303	1.039	1.08692	4.4
	308	1.035	1.08379	4.5
	313	1.031	1.08069	4.6
	318	1.028	1.07760	4.6
	323	1.024	1.07452	4.7
	328	1.021	1.07146	4.7
	333	1.017	1.06842	4.8
	338	1.013	1.06540	4.9
MAE	-	-	-	**4.6**
[BPyr][TFSI]	278	1.533	1.4125	7.9
	283	1.527	1.4078	7.8
	288	1.523	1.4032	7.9
	293	1.517	1.3987	7.8
	298	1.512	1.3942	7.8
	303	1.506	1.3897	7.7
	308	1.502	1.3852	7.8
	313	1.496	1.3807	7.7
	318	1.492	1.3763	7.8
	323	1.487	1.3718	7.7
	328	1.482	1.3672	7.7
	333	1.476	1.3629	7.7
	338	1.472	1.3585	7.7
	343	1.467	1.3540	7.7
	348	1.462	1.3496	7.7
	353	1.457	1.3453	7.7
	358	1.452	1.3409	7.7
	363	1.447	1.3366	7.6
MAE				**7.7**

Table 2. Experimental vs Calculated Density (g/cm^3)[1]

Ionic Liquid	OPLS	Experimental	% Error
[PrPyr][BF_4]	1.182	1.25308	5.6
[BPyr][BF_4]	1.154	1.21981	5.4
[OPyr][BF_4]	1.083	1.1127	3.0
[EPyr][DCA]	1.073	1.11849	4.1
[PrPyr][DCA][2]	1.058	1.09006	2.9
[BPyr][DCA]	1.043	1.06883	2.4
[PePyr][DCA]	1.028	1.05307	2.4
[HPyr][DCA]	1.016	1.03641	2.1
[EPyr][TFSI]	1.597	1.53560	4.0
[PrPyr][TFSI]	1.538	1.4800	3.9
[BPyr][TFSI]	1.512	1.45313	4.1
[PPyr][TFSI]	1.475	1.4214	3.8
[HPyr][TFSI]	1.443	1.38854	3.9
[OPyr][TFSI]	1.394	1.32815	5.0
MAE	-	-	**3.8**

Table 3. Experimental vs Calculated Surface Tension (mN/m)[3]

Ionic LIquid	OPLS	Experimental	% Error
[PrPyr][BF_4]	39.57	41.17	3.9
[BPyr][BF_4]	37.43	38.72	3.3
[EPyr][DCA]	51.85	50.56	2.6
[PrPyr][DCA]	47.23	49.70	4.0
[BPyr][DCA]	43.11	48.08	10.3
[PPyr][DCA]	39.35	45.29	13.1
[HPyr][DCA][4]	53.34	49.2	8.4
[EPyr][TFSI]	41.69	31.70	31.5
[BPyr][TFSI]	36.37	27.39	32.8
[PPyr][TFSI]	33.75	26.58	27.0
[HPyr][TFSI]	34.82	26.51	31.4
MAE	-	-	**15.3**

Table 4. Experimental vs Calculated Viscosity (cP)[1]

Ionic Liquid	OPLS	Experimental	% Error
[PrPyr][BF_4]	88.319	119.5	26.1
[BPyr][BF_4]	155.36	160.3	3.1
[OPyr][BF_4]	230.21	233.5	1.4
[EPyr][TFSI]	42.55	40.44	5.2
[PrPyr][TFSI]	27.68	27.6	0.3
[BPyr][TFSI]	60.70	60.2	0.8
[PPyr][TFSI]	71.61	71.9	0.4
[HPyr][TFSI]	85.46	94.06	9.1
[OPyr][TFSI]	110.53	114.9	3.8
MAE	-	-	**5.6**

[1] Calculated at 298 K unless otherwise noted
[2] Calculated at 313 K
[3] Calculated at 425 K unless otherwise noted
[4] Calculated at 298 K due to a lack of other data points to extrapolate to 425 K from.

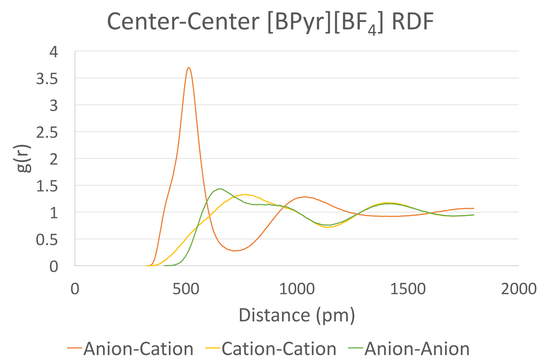


Figure 3. RDF of [BPyr][BF4] with respect to ion centers References for the ions in this RDF are the center of the pyridinium ring and the central boron atom of BPyr and BF4, respecitively.

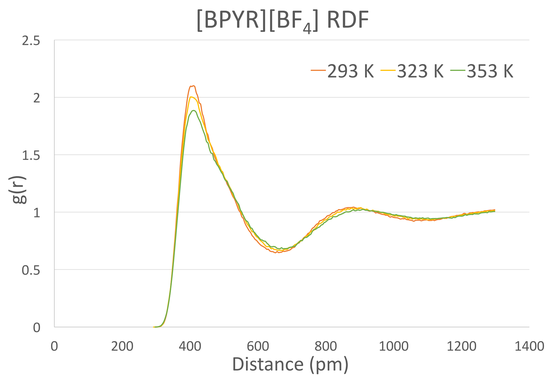


Figure 4. RDF of [BPyr][BF4] over a range of temperatures References for the ions in this RDF are the terminal carbon in the alkyl chain in two different BPyr cations.

Discussion

As can be seen from the comparison to experimental values, the OPLS force field implemented in GROMACS, in conjunction with the OPLS-2009IL parameters developed by the lab, is quite accurate in its predictions of the bulk properties of various ionic liquid systems. In addition, the modeling of the radial distribution function using our parameters appears to accurately model the local structural interactions of these systems. For example, in work by Sun et. al*, a graph with RDFs for center-center interactions for the same ion pairs found in Figure 3 corresponded closely with ours, showing a peak for anion-cation interactions at a distance of about 500 pm with a g(r) value of around 3.5 as well.

*Sun, H., Qiao, B., Zhang, D. and Liu, C.; *J. Phys. Chem.*, **2009**, *114*, 3990-3996

Future Work

- Test the ability of OPLS-2009IL to accurately determine heat capacity and heat of vaporization values of IL systems.
- Reexamine the parameters for the various TFSI systems and improve the predicted values.
- Use OPLS-2009IL to calculate the properties of systems containing other anions like PF_6 or NO_3

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