Thermodynamic, Structural and Dynamic Properties of Ionic Liquids [C_4mim][CF_3COO], [C_4mim] [Br] in condensed phase, using molecular simulations

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SUPPORTING MATERIAL

Force Field development

The classical Forcefields (FF) previously developed for the ILs studied in this work are based on the OPLS-AA [1] formalism using the following equation:

$$E = \sum_{bonds} k_r\,(r-r_0)^2 + \sum_{angles} k_\theta\,(\theta-\theta_0)^2 + \sum_{dihedrals} k_\chi\,[1+\cos(n\chi-\delta)] + \sum_{i<j}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{1}{4\pi\epsilon_0}\frac{q_iq_j}{r_{ij}}\right\} \tag{1}$$

where the parameters k_r, k_θ, and k_χ are the force constant for bonds, angles, and dihedrals, respectively; r, θ, and χ represent the distance between two bonded atoms, the angle between three consecutively bonded atoms, and the dihedral angle between four consecutively connected atoms, respectively. r_0, θ_0, n, and δ are the equilibrium bond, equilibrium angle, multiplicity and phase. ϵ_{ij} and σ_{ij} are the Lennard-Jones (LJ) parameters for each pair interaction, respectively; unlike parameters, i.e $i \neq j$, were calculated with the geometric combining rule. Electrostatic interactions are calculated using fixed atomic partial charges represented by q_i and q_j. All ion charges are less than ±1 e, as indicated in Table S1 and Table S2. Atomic partial charge are an important factor to be considered for the accurate representation of ILs using molecular simulations [2]. All 1-4 LJ and 1-4 coulombic interaction are scaled by a factor of 0.5 [1]. The complete list of parameters of the FF used in this work can be found in the Supporting Information section of the following references [3] [4]. A schematic representation of the [C_4mim][PF_6], [C_4mim][BF_4], [C_4mim][NTf_2], [C_4mim][CF_3COO], [C_4mim][Br], and [C_4mim][OMs] ILs is shown in Figure S1.

The all-atom (AA) FFs previously developed within the research group, were parameterized by using a methodology focused in the calculation of the atomic electrostatic charges employing an implicit solvent scheme to represent the condensed phase, and in the parametrization of the most representative dihedral angles by performing a simultaneous optimization between the classical FF energies obtained for the permissible molecular conformations, and the *ab-initio* molecular energies. The atomic partial charges were calculated, first by optimizing an IL dimer at the DFT M06 [5]/6-311++G(d,p) level of theory, in conjunction with the Solvation Model Density [6] incorporating the static dielectric constant for that IL, and later, by fitting the calculated charges using the Restricted Electrostatic Potential [7]

For more details about this methodology, the reader is referred to the following citation: [3]

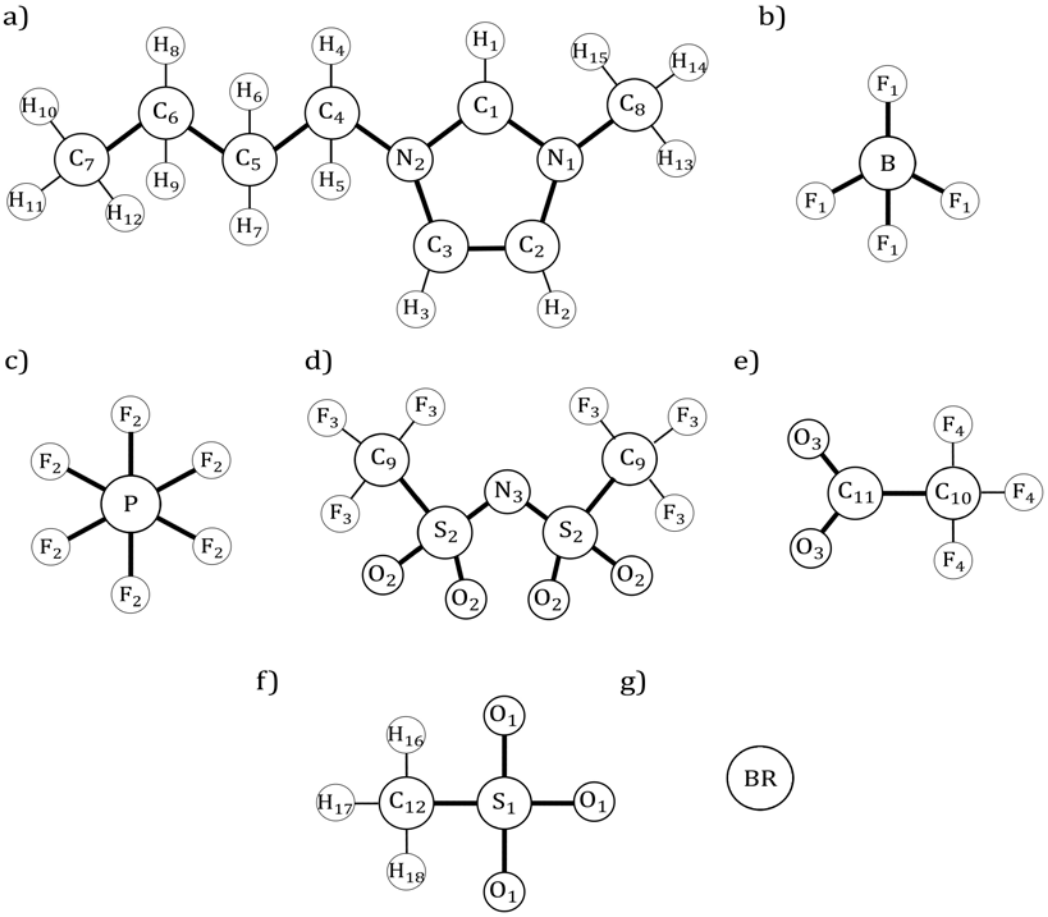

Figure S1. Schematic representation for all ILs studied: **a)** 1-Butyl-3-methylimidazolium cation $[C_4mim]^+$ **b)** Tetrafluoroborate anion $[BF_4]^-$ **c)** Hexafluorophosphate anion $[PF_6]^-$. **d)** Bis(trifluoromethylsulfonyl)imide anion $[NTf_2]^-$ **e)** Trifluoroacetate anion $[CF_3COO]^-$ **f)** Mesylate anion $[OMs]^-$ **g)** Bromide anion $[Br]^-$.

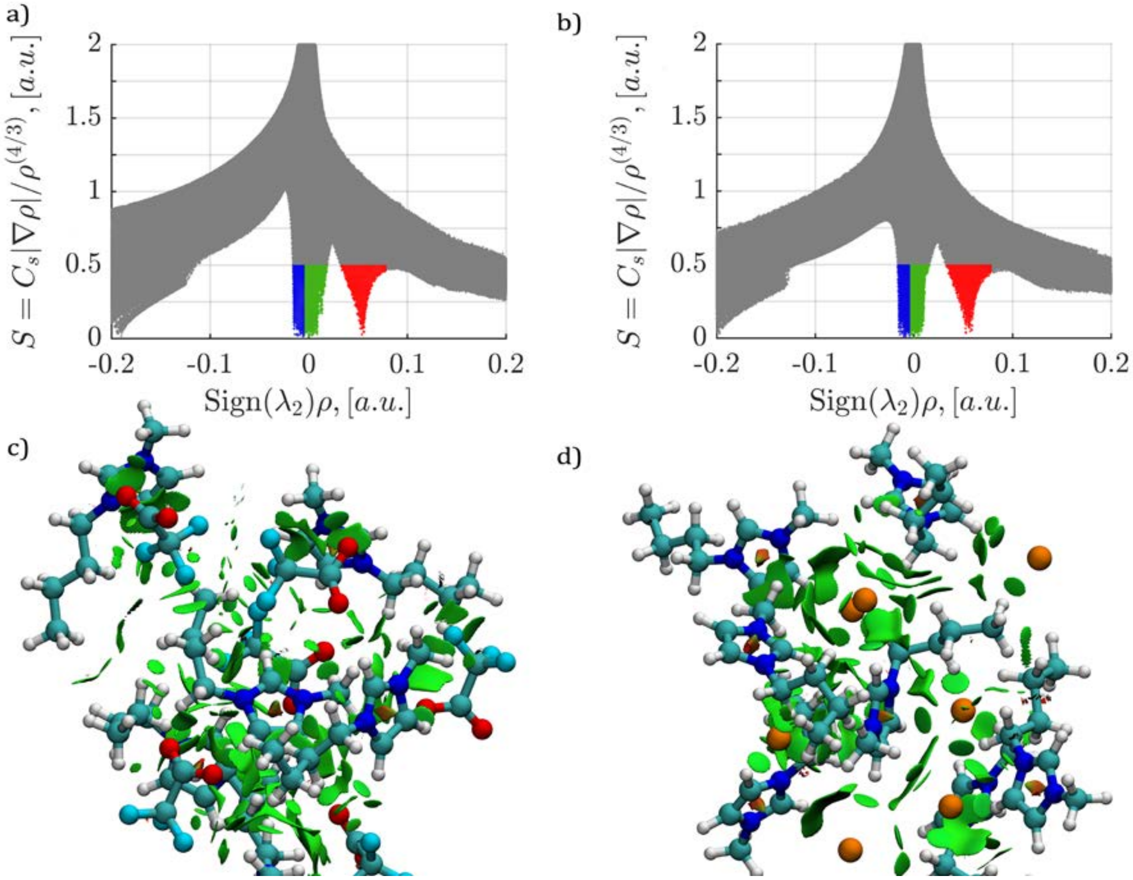

Figure S2. Plots of reduced density gradient (s) vs the electron density multiplied by the sign of the second Hessian eigenvalue Sign$(\lambda_2)\rho$ at 300 K. **a)** and **c)** results correspond to the [C_4mim][CF_3COO] IL; **c)** and **d)** results correspond to the [C_4mim][Br] IL. Attractive interactions are displayed in blue color, weak interactions in green color, and steric repulsions in red color. The isosurfaces correspond to a 0.5 a.u cutoff for s and the density color scale varies from $-0.10 < \rho < 0.10$ a.u. Steric repulsions are visualized within the center of the imidazolium ring.

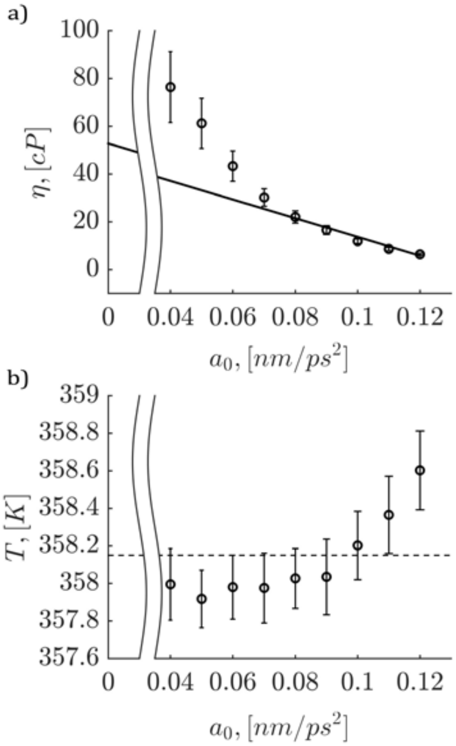

Figure S3. Viscosity calculation performed in this work for the [C_4mim][OMs] IL by using NEMD simulations at 358.15 K. All the plotted points include one standard deviation. **a)** Shear viscosity against acceleration amplitudes. The continuous line corresponds to the fitted weighted linear regression. **b)** Temperature against acceleration amplitudes. The dotted line corresponds to the target temperature of 358.15 K, fixed during all NEMD simulations.

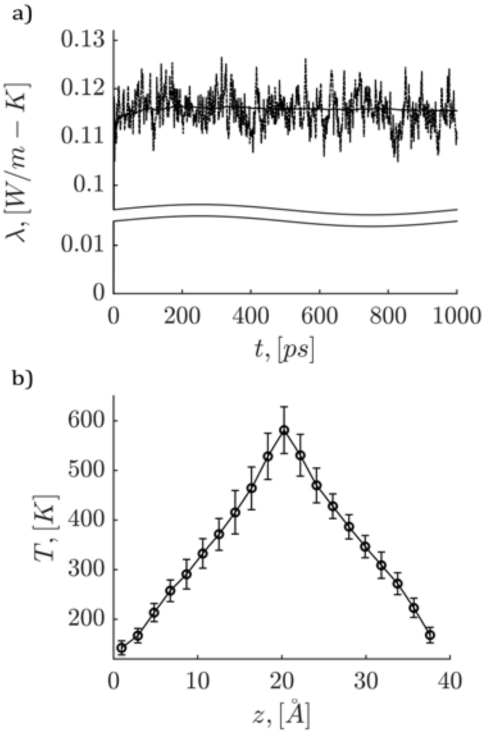

Figure S4. Thermal conductivity calculated for the [C_4mim][Br] IL in this work by using RNEMD simulations. **a)** Thermal conductivity as a function of simulation time. The thermal conductivity calculated at each step is displayed as dotted line. The time averaged value is displayed as continuous line. **b)** Temperature profile along the *z* box length. Each plotted point corresponds to the temperature reached in each slab, and includes one standard deviation.

Table S1. Atomic charges (*e*) for the IL studied[a,b,c]

Atom	[C$_4$mim][BF$_4$]	[C$_4$mim][PF$_6$]	[C$_4$mim][NTf$_2$]	[C$_4$mim][CF$_3$COO]	[C$_4$mim][OMs]	[C$_4$mim][Br]
$N_{1,2}$	0.1967	0.1938	0.2530	0.1705	0.2985	0.1583
N_3	---	---	-0.5874	---	---	---
C_1	-0.0656	-0.0417	-0.1649	-0.0238	-0.1893	0.0756
$C_{2,3}$	-0.2234	-0.2318	-0.2166	-0.2241	-0.2381	-0.2278
C_4	-0.3250	-0.2473	-0.3454	-0.2639	-0.3378	-0.3449
C_5	0.0738	0.0833	0.1592	0.0803	0.0353	0.0177
C_6	0.1667	0.1661	0.1017	0.1673	0.1843	0.1480
C_7	-0.3484	-0.3324	-0.4158	-0.2967	-0.3247	-0.3524
C_8	-0.2271	-0.2531	-0.2905	-0.3322	-0.3330	-0.2221
C_9	---	---	0.4618	---	---	---
C_{10}	---	---	---	0.5459	---	---
C_{11}	---	---	---	0.7034	---	---
C_{12}	---	---	---	---	-0.5944	---
H_1	0.2173	0.1957	0.2735	0.2193	0.2446	0.1266
$H_{2,3}$	0.2485	0.2557	0.2264	0.2451	0.2281	0.2536
$H_{4,5}$	0.1513	0.1278	0.1406	0.1311	0.1561	0.1587
$H_{6,7}$	0.0192	0.0037	-0.0034	0.0127	0.0212	0.0381
$H_{8,9}$	-0.0091	-0.0104	0.0130	-0.0123	-0.0127	0.0031
H_{10-12}	0.0834	0.0804	0.1069	0.0671	0.0747	0.0853
H_{13-15}	0.1283	0.1358	0.1389	0.1603	0.1468	0.1279
H_{16-18}	---	---	---	---	0.1912	---
B	0.9600	---	---	---	---	---
P		1.1714	---	---	---	---
F_1	-0.4633		---	---	---	---
F_2	---	-0.3447	---	---	---	---
F_3	---	---	-0.1564	---	---	---
F_4	---	---	---	-0.2392	---	---
S_1	---	---	---	---	1.2347	---
S_2	---	---	0.8273	---	---	---
O_1	---	---	---	---	-0.6880	---
O_2	---	---	-0.4834	---	---	---
O_3	---	---	---	-0.7051	---	---
BR	---	---	---	---	---	-0.8561
Total	±0.8932	±0.8968	±0.8812	±0.8785	±0.8501	±0.8561

[a] See atomic labels in Figure S1.

[b] Taken from previously published works in refs. [3] [4].

Table S2. Scaled atomic charges to ±0.8*e* for the [C_4mim][NTf_2], [C_4mim][CF_3COO], [C_4mim][Br], and [C_4mim][OMs] ILs studied in this work.[a,b,c]

Atom	[C_4mim][NTf_2]	[C_4mim][CF_3COO]	[C_4mim][OMs]	[C_4mim][Br]
$N_{1,2}$	0.2297	0.1553	0.2809	0.1479
N_3	-0.5332			
C_1	-0.1497	-0.0217	-0.1781	0.0706
$C_{2,3}$	-0.1966	-0.2041	-0.2240	-0.2129
C_4	-0.3136	-0.2404	-0.3178	-0.3223
C_5	0.1445	0.0731	0.0332	0.0165
C_6	0.0923	0.1524	0.1735	0.1383
C_7	-0.3775	-0.2702	-0.3056	-0.3293
C_8	-0.2637	-0.3026	-0.3134	-0.2075
C_9	0.4191			
C_{10}		0.4971		
C_{11}		0.6405		
C_{12}			-0.5594	
H_1	0.2483	0.1997	0.2302	0.1183
$H_{2,3}$	0.2055	0.2232	0.2147	0.2370
$H_{4,5}$	0.1276	0.1194	0.1469	0.1484
$H_{6,7}$	-0.0031	0.0116	0.0200	0.0356
$H_{8,9}$	0.0118	-0.0112	-0.0120	0.0029
H_{10-12}	0.0971	0.0611	0.0703	0.0797
H_{13-15}	0.1261	0.1460	0.1381	0.1195
H_{16-18}			0.1799	
B				
P				
F_1				
F_2				
F_3	-0.142			
F_4		-0.2178		
S_1			1.1619	
S_2	0.7511			
O_1			-0.6474	
O_2	-0.4388			
O_3		-0.6421		
BR				-0.8000

[a] See atomic labels in Figure S1.

[b] Scaled ±0.8 charges were used to calculate **<u>only</u>** the self-diffusion coefficient for this set of ILs.

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