Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Force field validation

To model the behavior of ionic liquids (IL) by molecular dynamics (MD) simulations, Canongia Lopes *et al.*[1,2] built a non-polarizable all-atom force field from quantum mechanical calculations. This force field is able to describe a large set of IL compounds, but it generally fails to reproduce quantitatively their transport properties. In particular, it typically overestimates their viscosity by one order of magnitude[3]. As quantitative results were expected from the present study, we implemented a standard charge scaling procedure[3,4] in order to properly reproduce the evolution of the density and of transport properties of the [mmIm$^+$][NTf$_2^-$] ionic liquid with the temperature. This modification was conducted following the method described by Chaban[5].

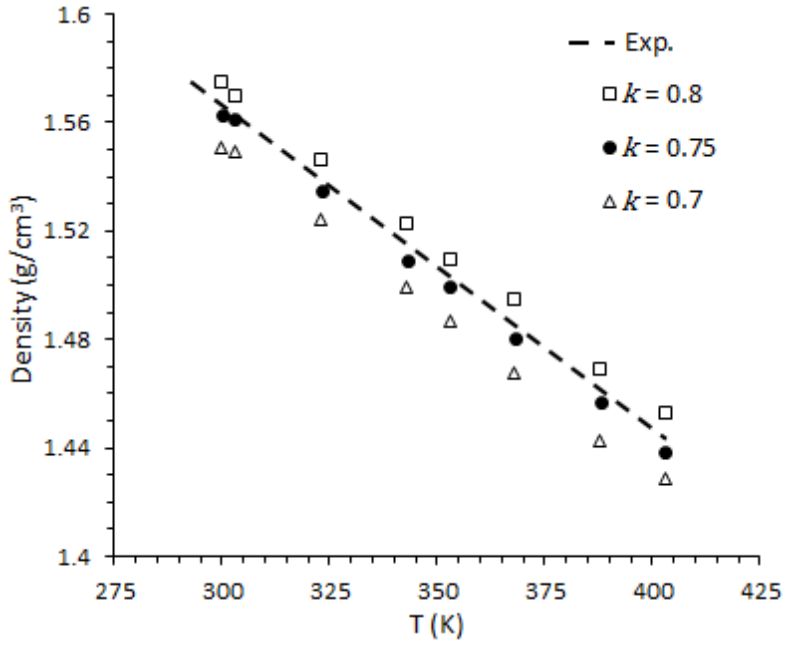


Figure 1. *Evolution of the bulk ionic liquid density with temperature, at ambient pressure p = 0.1 MPa. Symbols represent numerical values obtained for different weighting factors* k

applied to the Coulombic charges in the force field parameterization. The dashed line represents experimental results[5,6].

For this purpose, we computed the [mmIm$^+$][NTf_2^-] IL properties from MD simulations and compared them to experimental data. Fig.1 illustrates the variation of the IL density with temperature at ambient pressure p = 0.1 MPa, for both experimental data[5,6] and MD simulations carried out with 3 different weighting factors: k = 0.70, 0.75 and 0.80. The relative deviation between the computed density values and the measured ones is less than 1 % over the studied temperature range when $k = 0.75$. It was thus considered, for this specific k value, that density and by extension the structural properties of the [mmIm$^+$][NTf_2^-] ionic liquid were satisfactorily predicted.

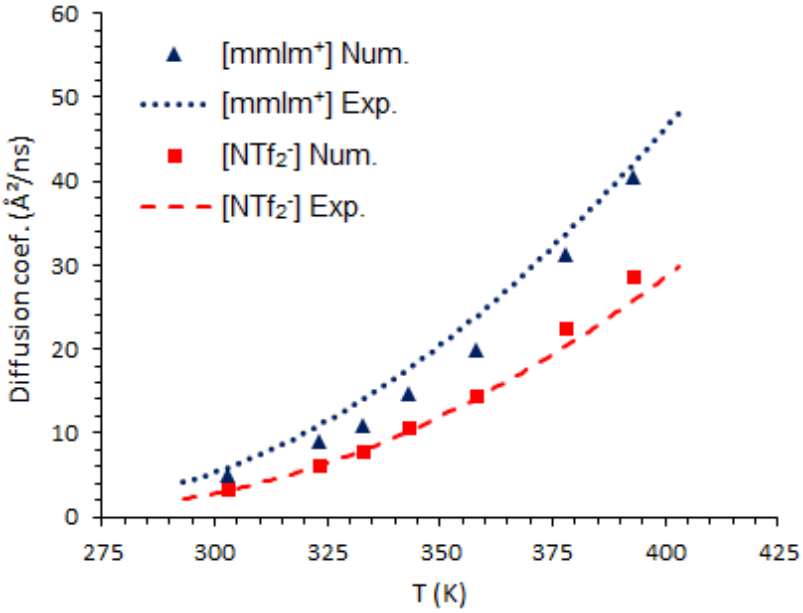


Figure 2. *Bulk diffusion coefficients of [mmIm+] cations (blue triangles) and [NTf_2-] anions (red squares) as a function of temperature, for a weighting factor k = 0.75 and at ambient pressure p = 0.1 MPa. Analytical laws determined empirically from experimental data*[7] *are plotted for comparison.*

As for dynamic properties, the diffusion coefficient was computed from the integration of the mean square displacement of the ions over time[8]. The weighting factor of 0.75 was used and

the results were compared with analytical predictions of empirical laws derived from experimental data[7]. Fig.2 shows the variation of the bulk diffusion coefficient of [mmIm$^+$] cations and [NTf$_2^-$] anions versus temperature, at ambient pressure p = 0.1 MPa. The agreement between the two set of results is fairly satisfying: the maximum relative deviations are of ca. 20 % for the cation and ca. 10 % for the anion at 333 and 393 K, respectively.

As a last step to confirm the k value of 0.75, the bulk shear viscosity at T = 303 K and p = 0.1 MPa was computed through equilibrium MD simulations using a Green-Kubo expression[8], still with the same weighting factor applied to the ions charges. The resulting viscosity value was equal to 36 ± 5 mPa.s, to be compared with the experimental one of 32 mPa.s[5], the relative deviation of 13 % being within the range of statistical errors. Finally, the choice of $k = 0.75$ appeared to be relevant to predict both density and transport properties of the [mmIm$^+$][NTf$_2^-$]: this weighting factor has thus been adopted in this study.

Force Field configuration

$$\boldsymbol{E_{total}} = \boldsymbol{E_{intermolecular}} + \boldsymbol{E_{bonds}} + \boldsymbol{E_{angles}}$$

$$\boldsymbol{E_{intermolecular}} = \sum 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}$$

For $r_{ij} < 12$ Å[a] and using Lorentz-Berthelot mixing rules for Lennard Jones coefficients. Within molecules, intermolecular interactions are weighted with the following factors:

- 0 for 1-bond separated atom
- 0 for 2-bonds separated atom
- 0.5 for more than 3-bonds separated atom

$$\boldsymbol{E_{bonds}} = \sum_{bonds} K_b(r$$

$$\boldsymbol{E_{angles}} = \sum_{angles} K_a(\theta$$

$$\boldsymbol{E_{dihedrals}} = \sum_{dihedrals} \frac{1}{2}V_1[1+\cos(\phi)] + \frac{1}{2}V_2[1-\cos(2\phi)] + \frac{1}{2}V_3[1+\cos(3\phi)]$$

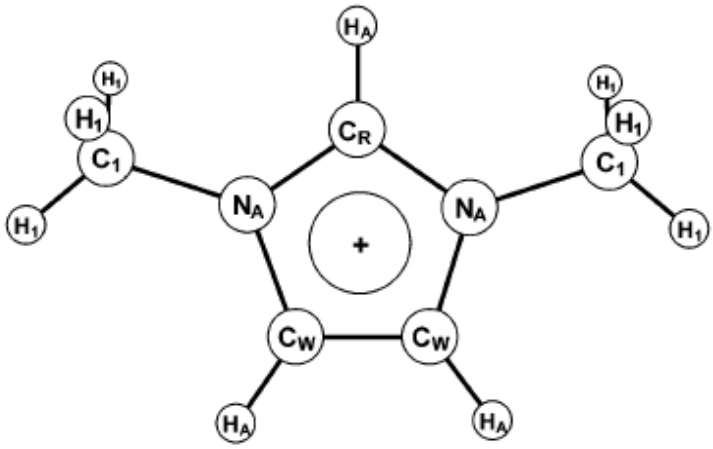
Coefficients

Iron(II) oxide [FeO]

L J + Coulomb	Mass (g/mol)	σ_{ij} (Å)	ϵ_{ij} (kcal/mol)	q_i (e)
Fe	55.845	4.9059	9.0298E-06	2
O	15.999	3.166	0.1554	-2

[a] Beyond 12 Å the Coulombic interactions are still effective but using a particle-particle particle-mesh solver[9]

1,3-dymethylimidazolium [mmIm$^+$]



L J + Coulomb	Mass (g/mol)	σ_{ij} (Å)	ϵ_{ij} (kcal/mol)	q_i (e)
N_A	14.0067	3.25	0.17	0.1125
C_R	12.011	3.55	0.07	-0.0825
C_W	12.011	3.55	0.07	-0.0975
C_1	12.011	3.5	0.065999	-0.1275
H_A	1.008	2.5	0.03	0.1575
H_1	1.008	2.5	0.03	0.0975

Bonds	r_0 (Å)	K_b (kcal/mol)
C_R-N	1.315	477.0555
C_W-N	1.378	427.1033
C_1-N	1.466	336.9981
C_R-H	1.08	339.762926[b]
C_W-H	1.08	339.762926[b]
C_W-C_W	1.341	520.076481
C_1-H	1.09	339.762926

[b] Coefficient values taken from the AMBER96 force field[10]

Angles	θ_0 (°)	K_a (kcal/mol)
C_W-N-C_R	108	69.93308
C_R-N-C_1	126.4	69.93308
C_W-N-C_1	125.6	69.93308
N-C_R-N	109.8	69.93308
N-C_R-H	125.1	34.96653
N-C_W-H	122	34.96653
N-C_W-C_W	107.1	69.93308
C_W-C_W-H	130.9	34.96653
N-C_1-H	110.7	74.8566
H-C_1-H	107.8	65.98948

Dihedrals	V_1 (kcal/mol)	V_2(kcal/mol)	V_3 (kcal/mol)
N-C_R-N-C_W	0	4.651	0
H-C_R-N-C_1	0	4.651	0
C_R-N-C_W-C_W	0	3	0
C_W-N-C_1-H	0	3	0
C_R-N-C_1-H	0	0	0
N-C_R-N-C_1	0	4.651	0
H-C_R-N-C_1	0	4.651	0
C_1-N-C_W-C_W	0	3	0
C_1-N-C_W-H	0	3	0
C_W-N-C_1-H	0	0	0.1314
N-C_W-C_W-N	0	10.75	0
N-C_W-C_W-H	0	10.75	0
H-C_W-C_W-H	0	10.75	0

Improper dihedrals	V_1 (kcal/mol)	V_2(kcal/mol)	V_3 (kcal/mol)
N	0	2.0004	0
$C_{R/W}$	0	2.1988	0

Bis(trifluoromethylsulfonyl)imide [NTf_2^-]

L J + Coulomb	Mass (g/mol)	σ_{ij} (Å)	ϵ_{ij} (kcal/mol)	q_i (e)
O	15.9994	2.96	0.21	-0.3975
S	32.065	3.55	0.25	0.765
F	18.998	2.95	0.053	-0.12
N	14.0067	3.25	0.17	-0.495
C	12.0107	3.5	0.066	0.2625

Bonds	r_0 (Å)	K_b (kcal/mol)
O-S	1.442	637.0545
N-S	1.57	372.0035
S-C	1.818	235.415
C-F	1.323	441.7915

Angles	θ_0 (°)	K_a (kcal/mol)
O-S-O	118.5	115.7955
O-S-N	113.6	94.2855
O-S-C	102.6	103.965
N-S-C	100.2	97.512
S-N-S	125.6	80.1845
S-C-F	111.8	82.933
F-C-F	107.1	93.3295

Dihedrals	V_1 (kcal/mol)	V_2(kcal/mol)	V_3 (kcal/mol)
O-S-N-S	0	0	-0.003585
O-S-C-F	0	4.651	0.34679
C-S-N-S	7.83294	-2.49044	-0.76362
N-S-C-F	0	0	0.31596

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