Thermodynamic Properties of Selected Homologous Series of Ionic Liquids Calculated Using Molecular Dynamics

Supporting Information

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1. FORCE FIELD PARAMETERS FOR THE $TFES^-$ ANION

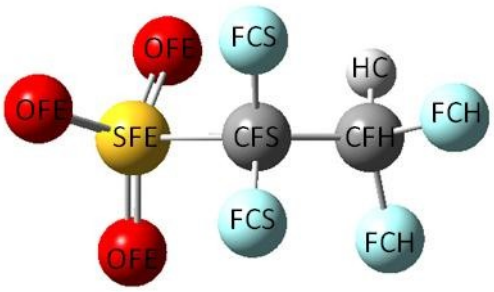

FIGURE S1. Mapping of atomic types in the $TFES^-$ anion.

TABLE S1

Force field parameters for the $TFES^-$ anion assembled in this work.

Atomic parameters					
$E_{vdW} = 4\varepsilon_{vdW}\left[\left(\frac{\sigma^0_{vdW}}{r}\right)^{12} - \left(\frac{\sigma^0_{vdW}}{r}\right)^{6}\right]$					
Atomic type	Atomic subtype	Mass / g mol^{-1}	Partial charge / e	σ^0_{vdW} / Å	ε_{vdW} / kcal mol^{-1}
CE	CFS	12.011	+0.25	3.50	0.066
CE	CFH	12.011	+0.41	3.50	0.066
HC	HC	1.008	+0.06	2.50	0.030
SE	SFE	32.065	+1.17	3.55	0.250
OE	OFE	15.999	–0.65	2.96	0.210
FE	FCS	18.998	–0.22	2.95	0.053
FE	FCH	18.998	–0.25	2.95	0.053
Bond parameters					
$E_{bond} = K_{bond}\left(d - d^0_{bond}\right)^2$					
Bond type	d^0_{bond} / Å	K_{bond} / kcal mol^{-1} Å^{-2}			
CE-CE	1.537	268.0			
CE-HC	1.087	340.0			
CE-SE	1.885	233.0			
SE-OE	1.459	637.1			
CE-FE	1.364	367.0			
Angle parameters					
$E_{angle} = K_{angle}\left(\phi - \phi^0_{angle}\right)^2$					
Angle type	ϕ^0_{angle} / deg	K_{angle} / kcal mol^{-1} deg^{-2}			
SE-CE-CE	112.9	69.97			
FE-CE-CE	109.2	50.00			
SE-CE-FE	110.2	82.93			

FE-CE-FE	106.9	77.00
CE-CE-HC	110.7	37.50
FE-CE-HC	109.3	48.76
OE-SE-CE	102.7	103.97
OE-SE-OE	115.3	115.80

Dihedral parameters

$$E_{\text{dihed}} = \frac{1}{2}\left[K_1\left(1+\cos\,\varphi\right)+K_2\left(1-\cos\,2\varphi\right)+K_3\left(1+\cos\,3\varphi\right)\right]$$

Dihedral type	K_1 / kcal mol^{-1}	K_2 / kcal mol^{-1}	K_3 / kcal mol^{-1}
SE-CE-CE-HC	0.0	0.0	0.3298
FE-CE-CE-HC	0.0	0.0	0.2900
SE-CE-CE-FE	0.0	0.0	0.3473
FE-CE-CE-FE	-2.5	0.0	0.2500
OE-SE-CE-CE	0.0	0.0	0.3331
OE-SE-CE-FE	0.0	0.0	0.3468
CW-CR-NA-CT	0.0	2.0005	0.0
NA-NA-CR-HA	0.0	2.1989	0.0
CR-CW-NA-CT	0.0	2.0005	0.0
NA-CW-CW-HA	0.0	2.1989	0.0
CW-NA-CW-HA	0.0	2.1989	0.0

2. CALCULATED VAPORIZATION ENTHALPIES

TABLE S2

Calculated $\Delta_{vap}H$ (in kJ mol^{-1}) for all 36 studied ILs at 4 selected temperatures.

The BF_4^- series				
Cation	350 K	400 K	450 K	500 K
$C_1C_1im^+$	177.6 ± 0.6	172.2 ± 0.8	167.4 ± 0.6	163.4 ± 0.7
$C_2C_1im^+$	175.7 ± 0.7	170.9 ± 0.7	165.7 ± 0.6	161.1 ± 0.5
$C_3C_1im^+$	176.4 ± 0.7	170.8 ± 0.6	165.9 ± 0.7	161.2 ± 0.6
$C_4C_1im^+$	178.6 ± 0.6	173.0 ± 0.7	167.1 ± 0.7	162.1 ± 0.7
$C_5C_1im^+$	182.1 ± 0.7	175.7 ± 0.7	169.8 ± 0.7	163.9 ± 0.8
$C_6C_1im^+$	187.0 ± 0.8	179.3 ± 1.0	173.2 ± 0.9	166.4 ± 0.9
$C_7C_1im^+$	191.1 ± 0.7	183.1 ± 0.8	175.8 ± 0.8	169.8 ± 0.9
$C_8C_1im^+$	195.4 ± 0.7	187.9 ± 0.8	180.3 ± 1.0	172.0 ± 1.0
$C_9C_1im^+$	199.8 ± 0.8	192.4 ± 1.1	184.9 ± 1.1	176.0 ± 1.0
$C_{10}C_1im^+$	205.3 ± 0.9	198.2 ± 0.9	189.9 ± 1.1	180.3 ± 1.0
$C_{11}C_1im^+$	211.3 ± 0.8	202.0 ± 1.0	193.1 ± 1.0	184.9 ± 1.0
$C_{12}C_1im^+$	217.4 ± 1.1	206.7 ± 1.1	197.6 ± 1.3	188.7 ± 1.2

The PF_6^- series				
Cation	350 K	400 K	450 K	500 K
$C_1C_1im^+$	183.9 ± 0.5	177.0 ± 0.6	173.7 ± 0.6	169.1 ± 0.6
$C_2C_1im^+$	182.5 ± 0.6	177.0 ± 0.6	171.7 ± 0.7	166.6 ± 0.7
$C_3C_1im^+$	184.1 ± 0.8	179.2 ± 0.9	172.8 ± 0.9	167.5 ± 0.9
$C_4C_1im^+$	186.5 ± 0.9	180.2 ± 0.7	174.4 ± 1.0	168.0 ± 0.8
$C_5C_1im^+$	188.8 ± 0.8	183.1 ± 0.8	176.3 ± 0.9	170.0 ± 0.9
$C_6C_1im^+$	193.4 ± 1.1	186.5 ± 1.1	179.0 ± 1.3	173.5 ± 1.6
$C_7C_1im^+$	197.6 ± 0.7	189.7 ± 0.9	182.9 ± 0.8	175.1 ± 0.9
$C_8C_1im^+$	201.8 ± 0.8	193.7 ± 0.9	186.2 ± 1.2	178.9 ± 1.3
$C_9C_1im^+$	206.0 ± 0.8	198.4 ± 0.9	189.8 ± 1 .0	182.1 ± 0.9
$C_{10}C_1im^+$	211.2 ± 0.8	202.4 ± 0.9	195.3 ± 0.9	187.2 ± 1.0
$C_{11}C_1im^+$	215.5 ± 1.0	207.9 ± 0.9	199.7 ± 1.0	190.7 ± 0.9
$C_{12}C_1im^+$	221.3 ± 0.8	213.1 ± 1.2	203.8 ± 1.1	194.9 ± 1.4
The $TFES^-$series				
Cation	350 K	400 K	450 K	500 K
$C_1C_1im^+$	177.3 ± 0.5	170.6 ± 0.6	164.4 ± 0.6	159.5 ± 0.8
$C_2C_1im^+$	176.5 ± 0.5	169.2 ± 0.7	163.2 ± 0.7	157.0 ± 0.7
$C_3C_1im^+$	178.0 ± 0.6	170.4 ± 0.6	163.8 ± 0.7	157.3 ± 0.8
$C_4C_1im^+$	180.5 ± 0.6	173.2 ± 0.8	166.0 ± 0.8	158.7 ± 0.8
$C_5C_1im^+$	183.9 ± 0.7	176.1 ± 0.7	168.7 ± 0.7	161.4 ± 0.8
$C_6C_1im^+$	187.7 ± 0.8	178.6 ± 0.9	171.3 ± 0.8	163.8 ± 1.0
$C_7C_1im^+$	192.6 ± 0.7	183.2 ± 0.8	175.2 ± 0.8	167.0 ± 0.9
$C_8C_1im^+$	197.0 ± 0.8	187.4 ± 0.8	179.2 ± 1.0	170.4 ± 1.0
$C_9C_1im^+$	201.7 ± 0.8	193.3 ± 0.9	183.4 ± 1.0	174.5 ± 1.1
$C_{10}C_1im^+$	206.1 ± 0.9	196.4 ± 0.8	188.0 ± 0.9	178.0 ± 1.4
$C_{11}C_1im^+$	211.7 ± 0.9	201.7 ± 1.0	191.2 ± 1.2	181.6 ± 1.0
$C_{12}C_1im^+$	216.6 ± 1.1	207.0 ± 1.5	196.0 ± 1.1	186.9 ± 1.1

3. POSITIONS OF THE FIRST MAXIMA OF THE RDF

TABLE S3
Positions of the first maxima (in Å) of several atom-atom types of RDFs for all 36 studied ILs at 2 selected temperatures.

The BF_4^- series										
	350 K					500 K				
Cation	N-N	CR-CR	B-B	N-B	CR-B	N-N	CR-CR	B-B	N-B	CR-B
$C_1C_1im^+$	6.2	6.3	6.5	4.5	3.9	6.4	6.6	6.7	4.6	4.0
$C_2C_1im^+$	6.5	6.7	6.7	4.5	3.9	6.7	7.3	7.0	4.9	4.3
$C_3C_1im^+$	7.0	7.4	6.9	4.6	3.9	7.3	7.5	7.3	4.6	4.0
$C_4C_1im^+$	7.5	7.5	6.9	4.6	3.9	7.8	8.0	7.2	4.6	4.0
$C_5C_1im^+$	7.9	6.8	6.8	4.5	3.8	8.0	7.9	7.3	4.6	3.9
$C_6C_1im^+$	6.9	6.5	6.8	4.6	3.9	7.4	7.5	7.2	4.6	3.9
$C_7C_1im^+$	7.0	6.7	6.8	4.5	3.8	7.3	7.1	7.0	4.6	3.9
$C_8C_1im^+$	6.8	6.6	6.7	4.5	3.9	7.0	7.4	7.0	4.6	3.9
$C_9C_1im^+$	6.8	6.4	6.6	4.5	3.9	7.0	6.9	7.1	4.6	4.0
$C_{10}C_1im^+$	6.3	6.4	6.0	4.5	3.8	6.7	6.7	7.0	4.6	3.9
$C_{11}C_1im^+$	6.5	6.4	6.7	4.5	3.9	6.6	6.5	6.9	4.6	3.9
$C_{12}C_1im^+$	6.3	6.3	6.7	4.5	3.9	6.5	6.6	7.0	4.5	3.9
The PF_6^- series										
	350 K					500 K				
Cation	N-N	CR-CR	P-P	N-P	CR-P	N-N	CR-CR	P-P	N-P	CR-P
$C_1C_1im^+$	6.5	6.5	6.7	4.8	4.2	6.7	7.0	7.0	4.9	4.3
$C_2C_1im^+$	7.0	7.7	6.9	4.9	4.2	7.1	7.8	7.3	4.9	4.3
$C_3C_1im^+$	7.2	7.3	7.3	4.9	4.2	7.3	7.8	7.4	5.0	4.3
$C_4C_1im^+$	7.4	7.8	7.1	4.9	4.2	7.7	7.8	7.5	5.0	4.3
$C_5C_1im^+$	7.5	8.1	7.2	4.9	4.2	7.9	8.0	7.5	4.9	4.3
$C_6C_1im^+$	7.5	8.0	7.0	4.9	4.2	7.9	8.1	7.5	4.9	4.3
$C_7C_1im^+$	7.3	8.0	7.0	4.8	4.2	7.6	7.9	7.4	4.9	4.3
$C_8C_1im^+$	7.2	7.9	7.1	4.9	4.2	7.7	8.0	7.5	4.9	4.3
$C_9C_1im^+$	7.1	7.9	6.9	4.8	4.2	7.3	7.9	7.3	4.9	4.2
$C_{10}C_1im^+$	7.0	7.9	7.0	4.9	4.2	7.2	7.7	7.3	4.9	4.3
$C_{11}C_1im^+$	6.9	7.0	7.0	4.8	4.2	7.1	7.9	7.3	4.9	4.3
$C_{12}C_1im^+$	7.0	6.7	7.0	4.9	4.2	7.1	7.2	7.2	4.9	4.3

The $TFES^-$ series										
	350 K					500 K				
Cation	N-N	CR-CR	S-S	N-S	CR-S	N-N	CR-CR	S-S	N-S	CR-S
$C_1C_1im^+$	6.3	6.6	7.0	4.6	3.9	6.3	6.6	7.0	4.6	3.9
$C_2C_1im^+$	6.6	7.0	7.3	4.7	4.0	7.2	7.9	7.5	4.8	4.1
$C_3C_1im^+$	7.2	7.5	7.5	4.7	4.0	7.8	7.8	7.8	4.8	4.1
$C_4C_1im^+$	9.4	8.1	7.4	4.7	4.0	9.1	8.1	8.0	4.8	4.1
$C_5C_1im^+$	7.1	7.8	7.2	4.7	4.0	9.4	8.1	7.7	4.7	4.1
$C_6C_1im^+$	7.1	7.4	7.2	4.7	3.9	7.8	7.9	7.7	4.8	4.2
$C_7C_1im^+$	6.6	6.9	7.2	4.6	3.9	7.2	7.5	7.5	4.7	4.0
$C_8C_1im^+$	6.4	6.4	6.9	4.6	3.9	6.7	7.2	7.5	4.7	4.0
$C_9C_1im^+$	6.4	6.4	7.1	4.6	4.0	6.9	7.2	7.3	4.7	4.1
$C_{10}C_1im^+$	6.4	6.3	6.9	4.6	3.9	6.7	7.2	7.5	4.7	4.1
$C_{11}C_1im^+$	6.2	6.3	7.1	4.7	4.0	6.5	6.9	7.5	4.7	4.1
$C_{12}C_1im^+$	6.2	6.2	7.0	4.6	3.9	6.6	7.1	7.4	4.7	4.0

4. MAXIMA OF THE SDF

For localization of the SDF maxima, let the $C_nC_1im^+$ cation be oriented in a way that the imidazolium ring lies in the *xy* plane, the *y* axis is identical with the axis of symmetry of the ring (not regarding the mutual asymmetry of the side chains) and pointing to the direction given by the CR type carbon atom; and the *x* axis points to the same direction from the ring as the longer side alkyl group. An illustration of the coordinate system orientation is given in Figure S2.

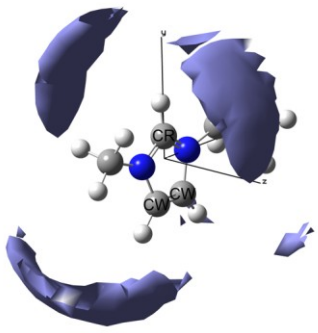

FIGURE S2. Orientation of the coordinate system around the $C_nC_1im^+$ cations.

TABLE S4

Two types of local maxima g_s^I and g_s^{II} and their relative positions (centers of given voxels x_{vo}, y_{vo}, z_{vo}) with respect to the center of the imidazolium ring of the anionic SDFs with respect to the $C_nC_1im^+$ cations for all 36 studied ILs at 350 K.

The BF_4^- series									
Cation	Type I maximum of SDF (g_s^I)				Type II maximum of SDF (g_s^{II})				Ratio g_s^I/g_s^{II}
	g_s^I	x_{vo}	y_{vo}	z_{vo}[a]	g_s^{II}	x_{vo}	y_{vo}	z_{vo}[a]	
$C_1C_1im^+$	16.2	0.4	7.4	–4.2	11.4	–7.1	–3.9	–4.2	1.42
$C_2C_1im^+$	19.2	–0.5	7.4	–4.2	13.6	–7.1	–4.8	–2.3	1.41
$C_3C_1im^+$	19.1	–0.5	7.4	–4.2	15.7	–7.1	–4.8	–2.3	1.21
$C_4C_1im^+$	20.7	–0.5	7.4	–4.2	18.8	–7.1	–4.8	–2.3	1.10
$C_5C_1im^+$	22.0	–0.5	7.4	–4.2	21.3	–8.1	–3.9	–2.3	1.03
$C_6C_1im^+$	23.3	–0.5	7.4	–4.2	23.3	–8.1	–3.9	–2.3	1.00
$C_7C_1im^+$	25.9	–0.5	7.4	–4.2	23.7	–7.1	–4.8	–2.3	1.09
$C_8C_1im^+$	28.7	–0.5	7.4	–4.2	25.2	–7.1	–4.8	–2.3	1.14
$C_9C_1im^+$	31.5	–0.5	7.4	–4.2	28.7	–8.1	–3.9	–2.3	1.10
$C_{10}C_1im^+$	32.3	–0.5	7.4	–4.2	30.5	–8.1	–3.9	–2.3	1.06
$C_{11}C_1im^+$	36.4	–0.5	7.4	–4.2	33.1	–7.1	–4.8	–2.3	1.10
$C_{12}C_1im^+$	35.1	–0.5	7.4	–4.2	34.6	–7.1	–4.8	–2.3	1.02
The PF_6^- series									
Cation	Type I maximum of SDF (g_s^I)				Type II maximum of SDF (g_s^{II})				Ratio g_s^I/g_s^{II}
	g_s^I	x_{vo}	y_{vo}	z_{vo}[a]	g_s^{II}	x_{vo}	y_{vo}	z_{vo}[a]	
$C_1C_1im^+$	19.9	0.4	6.5	–6.1	12.2	–7.1	–3.9	–5.1	1.63
$C_2C_1im^+$	22.9	–0.5	7.4	–4.2	14.3	–8.1	–4.8	–2.3	1.60
$C_3C_1im^+$	21.0	–0.5	8.4	–4.2	16.7	–8.1	–4.8	–2.3	1.26
$C_4C_1im^+$	23.4	–1.4	8.4	–4.2	20.5	–8.1	–4.8	–2.3	1.14
$C_5C_1im^+$	24.2	–0.5	6.5	–6.1	22.8	–8.1	–4.8	–2.3	1.06
$C_6C_1im^+$	27.3	–0.5	6.5	–6.1	24.9	–8.1	–4.8	–2.3	1.10
$C_7C_1im^+$	29.7	–0.5	6.5	–6.1	26.2	–8.1	–4.8	–2.3	1.13
$C_8C_1im^+$	29.5	–0.5	6.5	–6.1	28.2	–8.1	–4.8	–2.3	1.04

$C_9C_1im^+$	31.5	–0.5	6.5	–6.1	29.9	–8.1	–4.8	–2.3	1.05
$C_{10}C_1im^+$	37.5	–0.5	6.5	–6.1	33.0	–8.1	–4.8	–2.3	1.14
$C_{11}C_1im^+$	38.0	–0.5	6.5	–6.1	36.0	–8.1	–4.8	–2.3	1.06
$C_{12}C_1im^+$	39.4	–0.5	6.5	–6.1	36.5	–8.1	–4.8	–2.3	1.08
The $TFES^-$ series									
Cation	Type I maximum of SDF (g_s^I)				Type II maximum of SDF (g_s^{II})				Ratio g_s^I / g_s^{II}
	g_s^I	x_{vo}	y_{vo}	z_{vo}[a]	g_s^{II}	x_{vo}	y_{vo}	z_{vo}[a]	
$C_1C_1im^+$	16.9	0.4	5.5	7.1	10.6	–8.1	–4.8	–2.3	1.59
$C_2C_1im^+$	18.0	–0.5	7.4	–4.2	13.2	–8.1	–3.9	–3.2	1.36
$C_3C_1im^+$	16.6	–0.5	7.4	–4.2	14.8	–8.1	–3.9	–2.3	1.12
$C_4C_1im^+$	17.9	–0.5	7.4	–4.2	14.9	–8.1	–4.8	–1.4	1.20
$C_5C_1im^+$	20.6	0.4	7.4	–4.2	16.7	–8.1	–3.9	–3.2	1.23
$C_6C_1im^+$	22.4	–0.5	7.4	–4.2	17.3	–8.1	–3.9	–3.2	1.29
$C_7C_1im^+$	26.6	0.4	7.4	–4.2	18.9	–8.1	–3.9	–2.3	1.41
$C_8C_1im^+$	27.6	–0.5	7.4	–4.2	19.9	–8.1	–3.9	–2.3	1.39
$C_9C_1im^+$	28.5	–0.5	7.4	–4.2	21.5	–8.1	–3.9	–3.2	1.32
$C_{10}C_1im^+$	31.0	0.4	7.4	–4.2	23.4	–8.1	–3.9	–2.3	1.32
$C_{11}C_1im^+$	33.2	–0.5	7.4	–4.2	24.8	–8.1	–3.9	–2.3	1.34
$C_{12}C_1im^+$	32.0	0.4	7.4	–4.2	25.0	–8.1	–3.9	–2.3	1.28