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Supplementary

Vapor Pressure Mapping of Ionic Liquids and Low-Volatility Fluids using Graded Isothermal Thermogravimetric Analysis

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Table S1. Names, abbreviations, sources, molecular weights, decomposition temperatures, densities, viscosities, and typical water contents of scrupulously dry ionic liquids and other solvents studied.

Entry	Name	Abbreviation	MW (g/mol)	T_{dcp} [a] (K)	Source	d (g cm^{-3}) (293.15 K)	η (mPa·s) (298.15 K, 1 atm)	Water Content (ppm)
1	1-ethyl-3-methylimidazolium ethylsulfate	[C$_2$mIm][EtSO$_4$]	236.29	597.25	Prepared following ref. [1]	1.24[2]	0.9[2]	100–600
2	1-ethyl-3-methylimidazolium bis(pentafluoroethyl sulfonyl)imide	[C$_2$mIm][beti]	491.32	659.85	Prepared following our earlier study [3]	1.59 [4][b]	—	30–100
3	1-butyl-3-methylimidazolium bromide	[C$_4$mIm][Br]	219.13	532.35	Prepared following our earlier study [3]	—	—	100–600
4	1-butyl-3-methylimidazolium dicyanamide	[C$_4$mIm][dca]	204.28	526.65	Prepared following our earlier study [5]	1.06 [6][b]	30.04 [6]	100–600
5	1-butyl-3-methylimidazolium tetrafluoroborate	[C$_4$mIm][BF$_4$]	226.03	666.45	IoLiTec (IL-0012-HP-0100, 99%)	1.19	103.9 [7]	100–600
6	1-butyl-3-methylimidazolium hexafluorophosphate	[C$_4$mIm][PF$_6$]	284.19	673.85	IoLiTec (IL-0011-HP-0100, 99%)	1.37	132.3 [8]	30–100
7	1-butyl-3-methylimidazolium trifluoromethane sulfonate	[C$_4$mIm][TfO]	288.29	666.45	Prepared following our earlier study [3]	1.29 [6][b]	89.7 [6]	100–600
8	1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide	[C$_4$mIm][Tf$_2$N]	419.36	672.65	Prepared following our earlier study [3]	1.42 [9]	50.9 [2]	30–100
9	1-hexyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide	[C$_6$mIm][Tf$_2$N]	447.41	670.75	Prepared following our earlier study [3]	1.37 [6][b]	69.3 [6]	30–100
10	1-methyl-1-propylpyrrolidinium bis(trifluoromethyl sulfonyl)imide	[C$_3$mPy][Tf$_2$N]	408.37	698.55	Prepared following our earlier study [3,9]	1.40 [9]	61.5 [10]	30–100
11	1-butyl-1-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide	[C$_4$mPy][Tf$_2$N]	422.40	694.35	Prepared following our earlier study [9]	1.39 [9]	75.9 [6]	30–100
12	1-hexyl-1-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide	[C$_6$mPy][Tf$_2$N]	450.46	681.95	Prepared following our earlier study [9]	1.32 [9]	101 [11]	30–100
13	Isopropyl(dimethylpropyl) ammonium bis(trifluoromethyl sulfonyl)imide	[N$_{ip311}$][Tf$_2$N]	410.39	631.85	Prepared following our earlier study [9]	1.40 [9]	133	30–100
14	Hexyltrimethylammonium bis(trifluoromethyl sulfonyl)imide	[N$_{6111}$][Tf$_2$N]	424.42	665.25	Prepared following our earlier study [12]	1.31 [12][b]	153 [13]	30–100
15	Octyltrimethylammonium bis(trifluoromethyl sulfonyl)imide	[N$_{8111}$][Tf$_2$N]	452.47	661.25	Prepared following our earlier study [12]	1.27 [13]	356 [13]	30–100
16	Methyltrioctylammonium bis(trifluoromethyl sulfonyl)imide	[N$_{8881}$][Tf$_2$N]	648.85	647.35	Prepared following our earlier study [12]	1.08 [12][b]	—	30–100

17	Trihexyltetradecylphosphonium bis(trifluoromethyl sulfonyl)imide	[$P_{14,666}$][Tf_2N]	792.06	664.85	Prepared following our earlier study [14]	1.05 [12][b]	—	30–100
18	3,3′-(propane-1,3-diyl)bis(methyl-1H-imidazolium) bis(trifluoromethyl sulfonyl)imide	[$C_3(C_1Im)_2$][Tf_2N]$_2$	766.57	737.45	Prepared following our earlier study [15]	1.61 [16]	249 [16] (303.15 K)	30–100
19	Poly(butyl(4-ethylbenzyl)imidazolium chloride)	p([VBBIm][Cl])	278.82[c]	551.05	Prepared following ref. [17]	—	—	100–600
20	Poly(butylethylbenzylimidazolium bromide)	p([VBIm][Br])	233.15[c]	554.25	Prepared following ref. [17]	—	—	100–600
21	Poly(butylethylimidazolium bis(trifluoromethyl sulfonyl)imide)	p([VBIm][Tf_2N])	433.39[c]	618.65	Prepared following ref. [17]	—	—	30–100
22	Poly(ethylene glycol) 200	PEG 200	~200	462.75	Sigma-Aldrich (P3015)	1.124	~60	500–2000
23	Poly(ethylene glycol) 600	PEG 600	~600	630.55	Sigma-Aldrich (202401)	1.128	150–190	500–2000
24	Choline chloride:urea (1:2)	Reline	259.74	471.95	Prepared following our earlier study [18]	1.25 [19][b]	750 [19]	500–2000
25	Choline chloride:ethylene glycol (1:2)	Ethaline	263.76	444.15	Prepared following our earlier study [18]	1.12 [19][b]	37 [19]	500–2000
26	Choline chloride:glycerol (1:2)	Glyceline	323.80	517.75	Prepared following our earlier study [18]	1.18 [19][b]	259 [19]	500–2000
27	Tetrabutyl ammonium bromide/imidazole (3:7)	Bu_4NBr:Im	1443.70	420.75	Prepared following ref. [20]	—	810 [20]	500–2000
28	Propylammonium nitrate	PAN	122.12	516.65	Prepared following ref. [21]	1.16 [21][b]	63.7 [21]	500–2000
29	Triglyme	Triglyme	178.23	414.15	Sigma-Aldrich (T59803)	0.986[b]	1.95 [22]	500–2000
30	Lithium(triglyme) bis(trifluoromethanesulfonyl)imide	[Li(trigly)][Tf_2N]	465.30	529.65	Prepared as reported previously [23]	1.51 [23] (303.15 K)	169 [23] (303.15 K)	50–200
31	Glycerol	Gly	92.09	488.95	Sigma-Aldrich (G9012)	1.25	—	500–2000

[a] T_{dcp} is the decomposition temperature measured at the onset of decomposition (i.e., 10% mass loss following the initial plateau beyond the early mass loss). [b] density measured at 298.15 K. [c] Molar mass of monomer unit.

Table S2. The experimental evaporation rates of glycerol measured on two different commercial TGA instruments and the vapor pressures values taken from the literature.

T (K)	Trail-1		Trail-2		dm/dt-TGA-2 [b] (% min^{-1})	r^2	Literature P_{vap} (bar)	Ref.
	dm/dt-TGA-1 [a] (% min^{-1}),	r^2	dm/dt-TGA-1 [a] (% min^{-1})	r^2				
353.15	–	–	–	–	0.0055	0.9934	5.4599×10^{-5}	[24]
373.15	0.0492	0.9999	0.0328	0.9883	0.0305	0.9999	0.0003	[24]
393.15	0.1854	0.9999	0.1311	0.9987	0.0646	0.9999	0.0009	[24]
413.15	0.6568	0.9999	0.3600	0.9997	0.2127	0.9999	0.0032	[24]
433.15	1.8288	0.9999	0.9173	0.9999	0.7307	0.9999	0.0098	[24]
453.15	4.0349	0.9998	2.1427	0.9998	2.3861	0.9999	0.0257	[24]

[a] Measured on a TGA-Q50 V20.13 Build 39. [b] Measured on a Perkin Elmer TGA, Model 4000.

Table S3. Vapor pressure summary of ILs, DESs, and miscellaneous low-volatility conventional solvents at various temperatures.

Entry	ILs/DESs/molecular solvents	T (K)	Sample (mg)	Instrument	r^2	dm/dt (% min^{-1})	P_{vap} (Pa)
1	[C$_2$mIm][EtSO$_4$]	373.15	79.6	TGA-1	0.9997	0.0021	1.0364 ± 0.13
		393.15	78.7		0.9996	0.0108	5.9759 ± 0.55
		413.15	79.8		0.9994	0.0213	12.3597 ± 0.98
		433.15	78.8		0.9981	0.0370	22.3161 ± 1.54
2	[C$_2$mIm][beti]	463.15	101.4	TGA-1	0.9998	0.0004	0.1757 ± 0.02
		483.15	102.2		0.9999	0.0013	0.6202 ± 0.08
		503.15	100.6		0.9994	0.0044	2.2863 ± 0.25
		523.15	99.0		0.9999	0.0118	6.5699 ± 0.60
3	[C$_4$mIm][Br]	373.15	81.7	TGA-1	0.9649	0.0002	0.0837 ± 0.01
		393.15	81.2		0.9981	0.0003	0.1292 ± 0.02
		413.15	84.2		0.9999	0.0016	0.7746 ± 0.10
		433.15	83.1		0.9999	0.0075	4.0454 ± 0.40
4	[C$_4$mIm][dca]	373.15	68.6	TGA-1	0.9360	4.5720×10^{-5}	0.0173 ± 0.00
		393.15	64.1		0.9850	1.4960×10^{-4}	0.0614 ± 0.01
		413.15	64.5		0.9999	1.0000×10^{-3}	0.4684 ± 0.06
		433.15	64.8		0.9999	8.0000×10^{-3}	4.3346 ± 0.43
5	[C$_4$mIm][BF$_4$]	463.15	44.9	TGA-1	0.9976	2.0000×10^{-4}	0.0837 ± 0.01
		483.15	43.9		0.9986	9.0000×10^{-4}	0.4185 ± 0.06
		503.15	46.4		0.9999	1.9000×10^{-3}	0.9310 ± 0.11
		523.15	45.1		0.9999	6.0000×10^{-3}	3.1861 ± 0.33
6	[C$_4$mIm][PF$_6$]	463.15	61.6	TGA-1	0.9934	2.0000×10^{-4}	0.0837 ± 0.01
		483.15	55.4		0.9993	3.0000×10^{-4}	0.1292 ± 0.02
		503.15	51.3		0.9987	8.0000×10^{-4}	0.3689 ± 0.05
		523.15	49.0		0.9999	1.6000×10^{-3}	0.7746 ± 0.10
7	[C$_4$mIm][TfO]	483.15	83.1	TGA-1	0.9974	1.0000×10^{-4}	0.0399 ± 0.00
		503.15	82.6		0.9989	4.0000×10^{-4}	0.1757 ± 0.02
		523.15	83.8		0.9999	1.3000×10^{-3}	0.6202 ± 0.08
8	[C$_4$mIm][Tf$_2$N]	463.15	91.2	TGA-1	0.9990	3.4440×10^{-4}	0.1497± 0.02
		483.15	91.0		0.9999	5.6080×10^{-4}	0.2523 ± 0.04
		503.15	90.0		0.9999	2.0000×10^{-3}	0.9834 ± 0.12
		523.15	89.4		0.9999	4.0000×10^{-3}	2.0647 ± 0.23
9	[C$_6$mIm][Tf$_2$N]	463.15	83.5	TGA-1	0.9990	2.0570×10^{-4}	0.0863 ± 0.01
		483.15	86.4		0.9999	4.7430×10^{-4}	0.2109 ± 0.03
		503.15	88.5		0.9999	1.0000×10^{-3}	0.4684 ± 0.06
		523.15	88.1		0.9999	4.0000×10^{-3}	2.0647 ± 0.23
10	[C$_3$mPy][Tf$_2$N]	463.15	89.7	TGA-1	0.9810	1.3020×10^{-5}	0.0045 ± 0.00
		483.15	89.7		0.9990	7.4760×10^{-5}	0.0292 ± 0.00
		503.15	90.3		0.9999	1.9650×10^{-4}	0.0821 ± 0.01
		523.15	89.3		0.9999	4.5240×10^{-4}	0.2005 ± 0.03
11	[C$_4$mPy][Tf$_2$N]	473.15	21.7	TGA-1	0.9223	4.1301×10^{-5}	0.0155 ± 0.00
		493.15	20.7		0.9960	2.0000×10^{-4}	0.0837 ± 0.01
		513.15	21.7		0.9969	2.0000×10^{-4}	0.0837 ± 0.01
		533.15	23.4		0.9997	7.0000×10^{-4}	0.3198 ± 0.04
		553.15	24.9		0.9995	1.7000×10^{-3}	0.8265 ± 0.11
12	[C$_6$mPy][Tf$_2$N]	463.15	83.7	TGA-1	0.9958	3.2583×10^{-5}	0.0120 ± 0.00
		483.15	83.0		0.9967	5.8460×10^{-5}	0.0224 ± 0.00
		503.15	83.8		0.9998	2.0000×10^{-4}	0.0837 ± 0.01
		523.15	83.8		0.9999	6.0000×10^{-4}	0.2712 ± 0.04
13	[N$_{ip311}$][Tf$_2$N]	463.15	88.4	TGA-1	0.9946	3.2962×10^{-5}	0.0122± 0.00
		483.15	90.2		0.9996	1.0000×10^{-4}	0.0399 ± 0.00
		503.15	89.8		0.9992	7.0000×10^{-4}	0.3198 ± 0.04
		523.15	89.0		0.9990	4.2000×10^{-3}	2.1753 ± 0.24
14	[N$_{6111}$][Tf$_2$N]	463.15	85.3	TGA-1	0.9997	6.0000×10^{-4}	0.2712 ± 0.04
		483.15	84.6		0.9989	9.0000×10^{-4}	0.4185 ± 0.06
		503.15	90.0		0.9994	1.8000×10^{-3}	0.8786 ± 0.11
		523.15	84.9		0.9999	1.9000×10^{-3}	0.9309 ± 0.11
15	[N$_{8111}$][Tf$_2$N]	463.15	81.4	TGA-1	0.9994	1.1900×10^{-3}	0.5643 ± 0.08
		483.15	81.3		0.9987	1.2480×10^{-3}	0.5937 ± 0.08
		503.15	81.1		0.9978	2.7000×10^{-3}	1.3558 ± 0.16
16	[N$_{8881}$][Tf$_2$N]	463.15	68.2	TGA-1	0.9878	1.0000×10^{-4}	0.0399 ± 0.00
		483.15	68.6		0.9984	2.0000×10^{-4}	0.0837 ± 0.01
		503.15	68.5		0.9999	1.1000×10^{-3}	0.5187 ± 0.07
		523.15	68.0		0.9999	4.9000×10^{-3}	2.5654 ± 0.27
17	[P$_{14,666}$][Tf$_2$N]	463.15	65.9	TGA-1	0.9986	8.0000×10^{-4}	0.3689 ± 0.05
		483.15	65.6		0.9932	3.0000×10^{-4}	0.1292 ± 0.02
		503.15	66.6		0.9987	4.0000×10^{-4}	0.1757 ± 0.02
		523.15	66.6		0.9999	1.0000×10^{-3}	0.4684 ± 0.06
18	[C$_3$(C$_1$Im)$_2$] [Tf$_2$N]$_2$	573.15	28.9	TGA-1	0.9997	0.0009	0.4185 ± 0.06

		585.15	26.1		0.9995	0.0031	1.5718 ± 0.18
		605.15	31.6		0.9992	0.0087	4.7416 ± 0.45
		623.15	32.1		0.9997	0.0300	17.8305 ± 1.3
		423.15	27.1		0.9942	0.0012	1.1835 ± 43
19	p([VBBIm]Cl)	443.15	27.7	TGA-2	0.9974	0.0027	2.7507 ± 0.91
		463.15	32.8		0.9988	0.0079	8.4014 ± 2.39
		483.15	26.8		0.9976	0.0241	26.7989 ± 6.41
		403.15	14.8		0.9780	0.0002	0.1003 ± 0.01
20	p([VBIm]Br)	423.15	18.7	TGA-1	0.9960	0.0005	0.2135 ± 0.03
		443.15	15.6		0.9900	0.0010	0.4684 ± 0.06
		463.15	22.1		0.9999	0.0030	1.5176 ± 0.18
		463.15	5.2		0.9970	0.0020	0.9834 ± 0.12
21	p([VBIm][Tf_2N])	483.15	8.1	TGA-1	0.9970	0.0030	1.5176 ± 0.17
		503.15	11.0		0.9999	0.0060	3.1861 ± 0.33
		523.15	6.5		0.9999	0.0340	20.3857 ± 1.44
		373.15	70.7		0.9999	0.0577	35.9005 ± 2.17
22	PEG 200	393.15	72.1	TGA-1	0.9995	0.1490	99.0723 ± 4.26
		413.15	71.1		0.9991	0.3484	245.8749 ± 7.15
		433.15	73.1		0.9993	0.8807	663.1456 ± 13.40
		373.15	32.3		0.9962	0.0015	1.4926 ± 0.53
23	PEG 600	393.15	30.7	TGA-2	0.9996	0.0042	4.3551 ± 1.40
		413.15	31.1		0.9956	0.0022	2.2230 ± 0.76
		433.15	31.4		0.9969	0.0070	7.4083 ± 2.15
		353.15	29.3		0.9974	0.0021	2.1180 ± 0.73
24	Reline	373.15	28.0	TGA-2	0.9980	0.0071	7.5184 ± 2.18
		393.15	32.2		0.9997	0.0264	29.4637 ± 6.94
		413.15	25.5		0.9972	0.0888	104.0324 ± 20.05
		313.15	37.8		0.9977	0.0077	8.1803 ± 2.34
		323.15	34.1		0.9999	0.0174	19.0981 ± 4.81
25	Ethaline	333.15	31.0	TGA-2	0.9995	0.0339	38.2144 ± 8.64
		343.15	35.5		0.9994	0.0521	59.7489 ± 12.60
		353.15	37.3		0.9990	0.0812	94.7889 ± 18.54
		373.15	28.1		0.9997	0.0066	6.9686 ± 2.04
26	Glyceline	393.15	29.2	TGA-2	0.9999	0.0247	27.4931 ± 6.55
		413.15	29.5		0.9996	0.0684	79.3008 ± 15.96
		433.15	31.8		0.9983	0.1359	161.9449 ± 29.18
		333.15	28.6		0.9956	0.0027	2.7507± 0.91
27	Bu_4NBr:Im (3:7)	353.15	30.6	TGA-2	0.9999	0.0088	9.3990 ± 2.63
		373.15	30.7		0.9994	0.0264	29.4637 ± 6.94
		393.15	29.8		0.9980	0.0638	73.7620 ± 15.04
		353.15	28.3		0.9158	0.0003	0.2799 ± 0.12
28	PAN	373.15	29.8	TGA-2	0.9942	0.0009	0.8775 ± 0.35
		393.15	32.3		0.9991	0.0029	2.9629 ± 0.97
		413.15	27.2		0.9997	0.0186	20.4697 ± 5.10
		313.15	38.9		0.9996	0.0543	62.3750 ± 13.04
		323.15	39.1		0.9998	0.0894	104.7635 ± 20.17
29	Triglyme	333.15	31.0	TGA-2	0.9996	0.1530	183.1885 ± 32.41
		343.15	33.2		0.9998	0.2024	245.0631 ± 41.64
		353.15	31.8		0.9985	0.4717	590.7878 ± 91.35
		353.15	31.4		0.9971	0.0022	2.2230 ± 0.76
30	[Li(trigly)][Tf_2N]	373.15	33.2	TGA-2	0.9979	0.0059	6.2016 ± 1.84
		393.15	35.8		0.9977	0.0128	13.8777 ± 3.67
		413.15	33.9		0.9972	0.0236	26.2209 ± 6.29

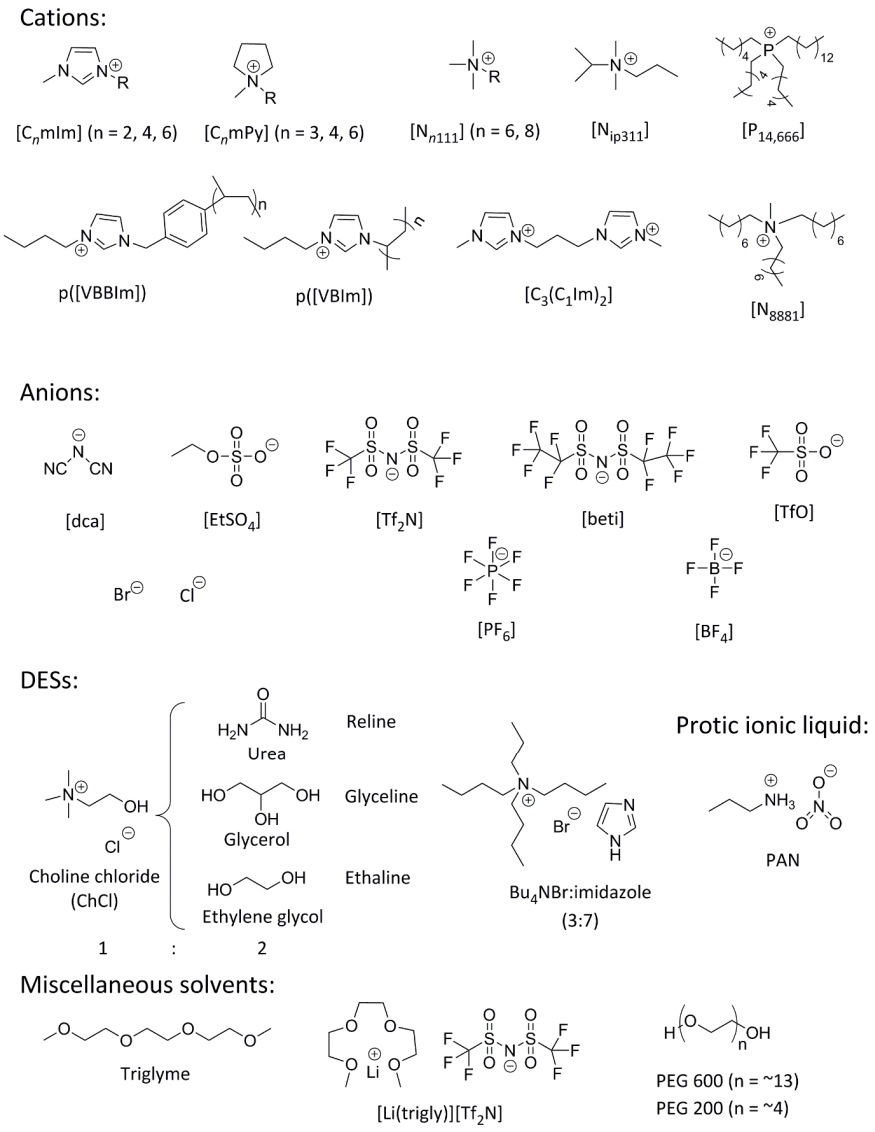

Figure S1. Summary of cations, anions, DESs, and other solvents studied and their abbreviations (R = alkyl group).

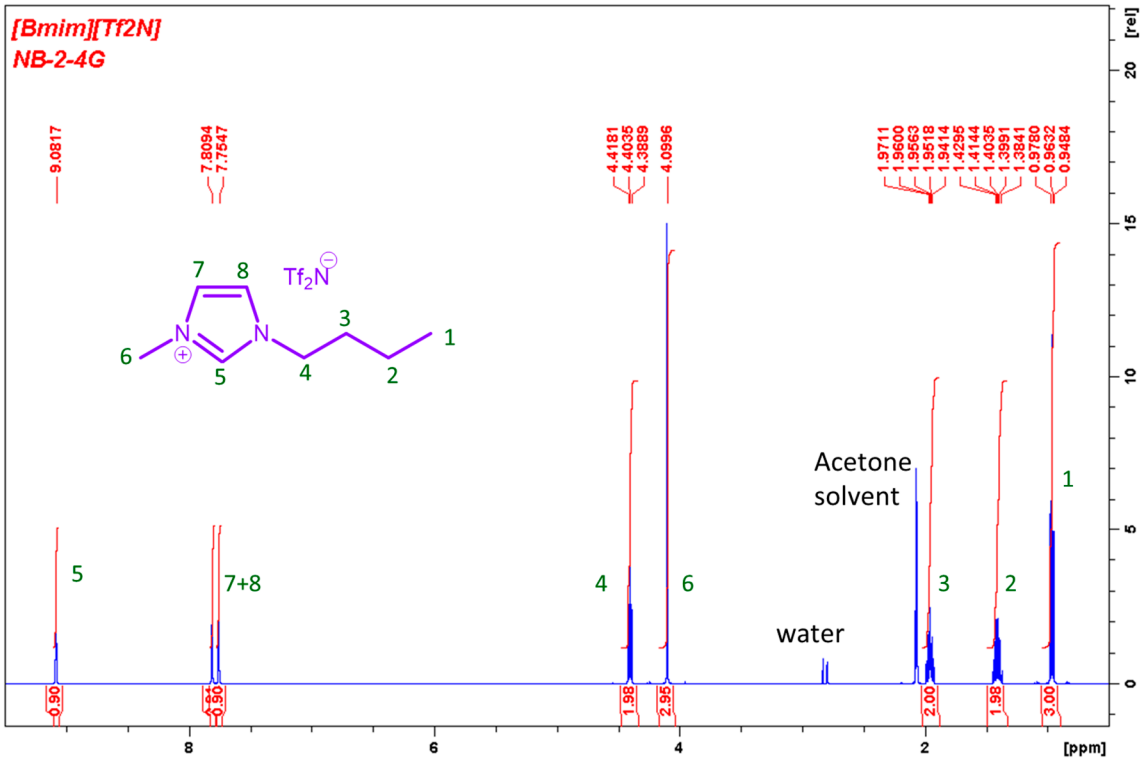

Figure S2. Representative ^{1}H-NMR spectrum for [C4mIm][Tf2N] using deuterated acetone as the solvent. Peaks are assigned numerically beside the molecule.

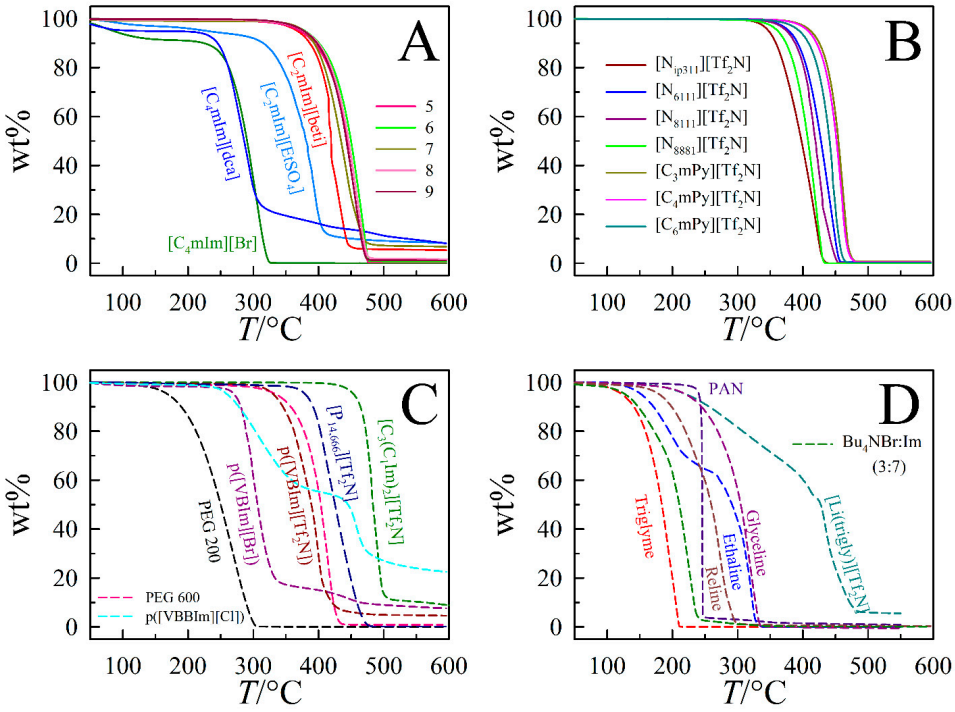

Figure S3. Thermal stabilities of 30 liquids. (**A**) [C4mIm]-based ILs with different anionic structures (5: [C4mIm][BF4]; 6: [C4mIm][PF6]; 7: [C4mIm][TfO]; 8: [C4mIm][Tf2N]; 9: [C6mIm][Tf2N]); (**B**) ammonium-, and pyrrolidinium-based Tf2N ILs; (**C**) PEGs, dicationic ILs, [P14,666][Tf2N], and polymeric ILs; (**D**) protic IL, triglyme, and DESs.

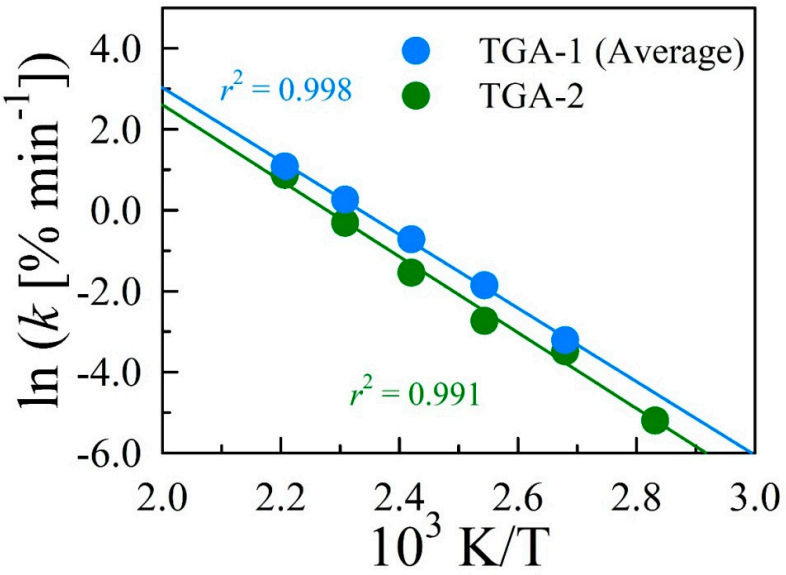

Figure S4. Comparison of experimental evaporation rates of glycerol measured on two commercial instruments (TGA-1 and TGA-2) at various temperatures. The evaporation rate of glycerol from both instruments are comparable with each other and are used to estimate the instrument coefficients (*a* and *b*).

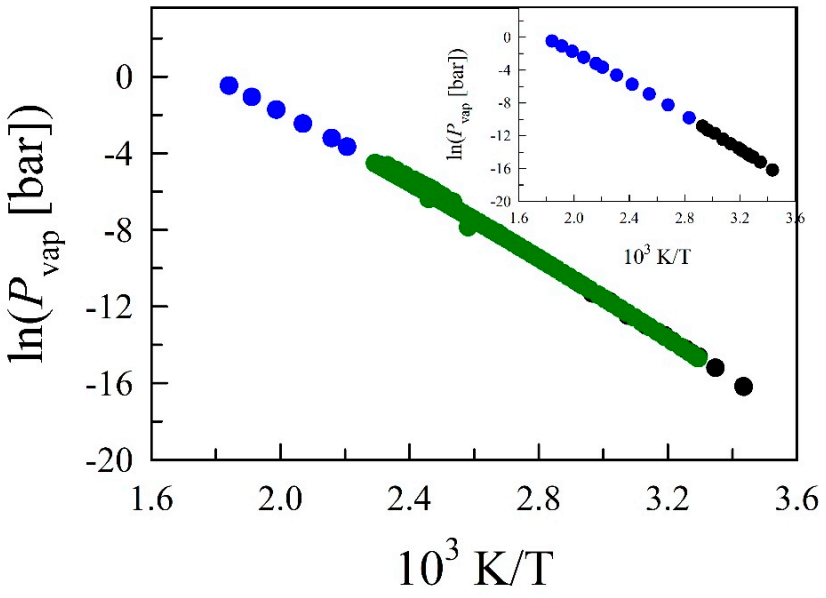

Figure S5. P_{vap} values of pure glycerol obtained from the literature (blue: ref [24], dark green: ref. [25], and black: ref. [26]. All P_{vap} data obtained from different studies at different temperatures correlate with each other, suggesting the P_{vap} values are consistent and reliable. P_{vap} values used in this study originate from ref. [24].

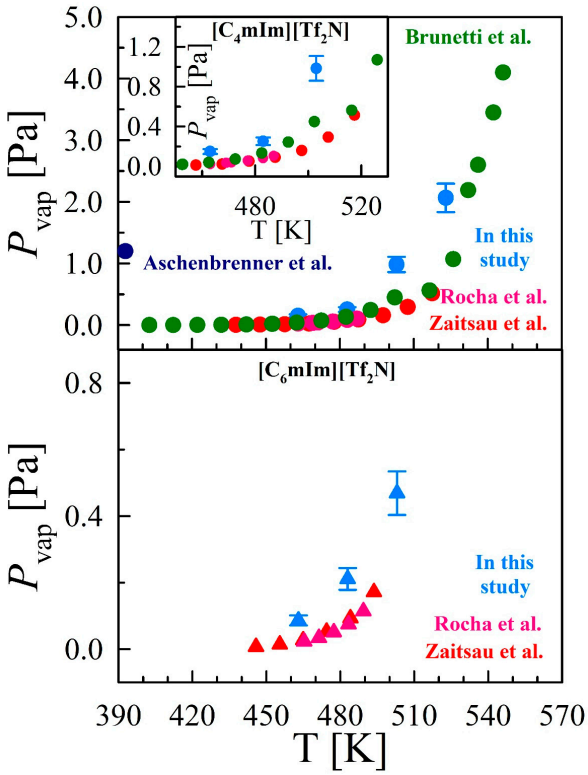

Figure S6. Correlation between present and literature P_{vap} values with respect to temperature. (Upper) [C4mim][Tf2N] (Zaitsau et al. [27], Rocha et al. [28], Aschenbrenner et al. [29], and Brunetti et al. [30]). (Lower) [C6mim][Tf2N] (Zaitsau et al. [27] and Rocha et al. [28]).

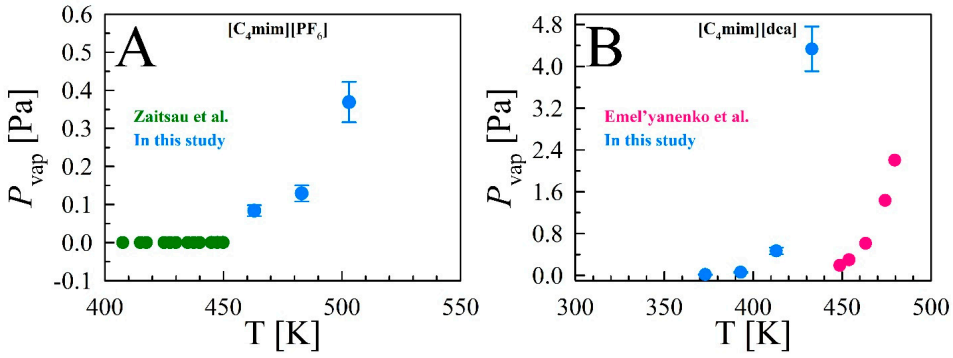

Figure S7. Comparison of P_{vap} results with literature data as function of temperature. (**A**) [C4mim][PF6] (Zaitsau et al. [31]), (**B**) [C4mim][dca] (Emel'yanenko et al. [32]).

In Figure S7A, the P_{vap} data measured in this study for [C4mim][PF6] are in the range of 0.084–0.775 Pa at 463–523 K, which are in line with Zaitsau et al. [31] values measured at 407–455 K using QCM method. However, the P_{vap} data measured for [C4mim][dca] are higher than the literature values measured by Emel'yanenko et al. [32] using the transpiration method, see Figure S7B. The evaporated mass in this study at 373–433 K is 6–8%, which is much lower than the value (2–20%) reported in Rui et al. [33], signifying the purity of the IL. Further, the exponential rise in P_{vap} value at 433 K indicates that the probability of proton transfer from the cation to [dca$^-$] anion increases with temperature giving rise to a neutral ion pair. In addition, the decomposition of [C4mim][dca] occurs before 473 K, illustrating the results presented here are acceptable. Overall, the data provided here provide evidence that out TGA method is sufficiently reliable for measuring thermal properties of ILs.

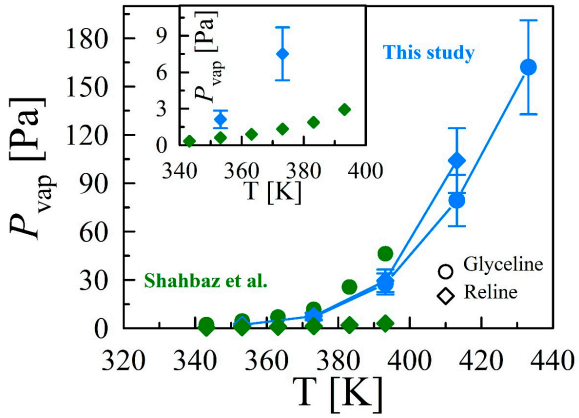

Figure S8. P_{vap} results of glyceline (circles) and reline (rhombus) DESs mixtures in comparison with Shahbaz et al. [34]. This study (blue) and Shahbaz et al. (green) were measured using TGA. Inset shows the values of reline measured by Shahbaz et al.

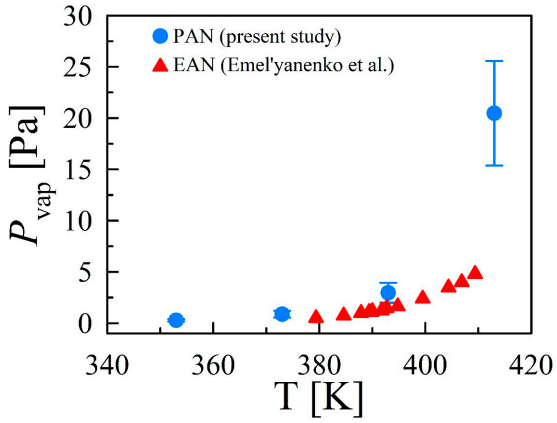

Figure S9. P_{vap} plot of PAN (as measured in this study) and EAN (as measured by Emel'yanenko et al. [35]) as a function of temperature.

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