

# Supplementary Information

## Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide and arenes<sup>♦</sup>

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**Keywords:** ionic liquids; liquid-liquid equilibria; aromatic solvents; pressure effects

**Table S1** Liquid-liquid phase equilibria data of  $[C_n\text{mim}][\text{NTf}_2]$  + benzene;  $n$  is the number of carbon atoms in the alkyl chain of the substituted imidazolium;  $x_{\text{IL}}$  and  $w_{\text{IL}}$  are the mole and weight fraction of ionic liquid, respectively, and  $T$  is the temperature of transition.

$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$
<b><math>n = 2</math></b>								
0.22927	0.59844	300.58	0.23809	0.61022	343.15	0.24222	0.61559	360.91
0.23431	0.60523	324.03						
<b><math>n = 4</math></b>								
0.17802	0.53763	335.55	0.18009	0.54112	300.58	0.19727	0.56885	459.42
0.17802	0.53763	422.87	0.18493	0.54916	280.18			
<b><math>n = 6</math></b>								
0.00356	0.02007	390.55	0.10540	0.40292	400.68	0.12080	0.44039	330.28
0.00540	0.03016	431.19	0.10540	0.40292	458.15	0.12080	0.44039	482.63
0.00631	0.03512	451.18	0.11215	0.41979	368.13	0.12761	0.45589	297.71
0.00631	0.03512	484.38	0.11215	0.41979	473.59			
<b><math>n = 8</math></b>								
0.00171	0.01030	300.32	0.02245	0.12263	372.66	0.05183	0.24965	361.07
0.00263	0.01577	324.52	0.02724	0.14563	374.05	0.05846	0.27428	352.73
0.00521	0.03090	348.20	0.02833	0.15073	374.31	0.06670	0.30315	338.10
0.00985	0.05712	361.72	0.03379	0.17552	373.93	0.08075	0.34841	312.59
0.01416	0.08040	368.25	0.03931	0.19938	371.27	0.08667	0.36615	300.32
0.01805	0.10065	370.57	0.04538	0.22444	367.95			
<b><math>n = 10</math></b>								
0.00337	0.02133	300.84	0.01361	0.08167	318.23	0.02280	0.13075	317.94
0.00430	0.02706	305.82	0.01465	0.08746	318.23	0.02352	0.13440	317.81
0.00511	0.03205	309.37	0.01506	0.08972	318.36	0.02454	0.13955	317.87
0.00566	0.03542	310.85	0.01558	0.09257	318.48	0.02562	0.14491	317.53
0.00677	0.04210	312.83	0.01639	0.09687	318.44	0.02847	0.15888	316.89
0.00759	0.04696	314.78	0.01724	0.10159	318.50	0.03239	0.17749	315.32*
0.00844	0.05199	315.66	0.01790	0.10514	318.58	0.03272	0.17900	314.79
0.00891	0.05478	316.02*	0.01874	0.10961	318.27	0.03745	0.20051	311.94
0.00931	0.05709	316.37	0.01878	0.10980	318.54	0.04044	0.21365	309.08
0.01020	0.06231	317.11	0.01978	0.11508	318.46	0.04378	0.22788	305.77
0.01104	0.06712	317.44	0.01978	0.11510	318.29*	0.04583	0.23644	302.45
0.01184	0.07172	317.79	0.02062	0.11950	318.18	0.04671	0.24003	301.30
0.01187	0.07184	317.71*	0.02074	0.12013	318.30	0.04729	0.24242	300.60
0.01280	0.07710	317.71	0.02157	0.12442	318.17			
0.01280	0.07716	318.17	0.02241	0.12877	317.95			

\* values obtained from linear extrapolation of  $T = f(p)$  to a nominal pressure of 0.1 MPa.

**Table S2** Liquid-liquid phase equilibria data of  $[C_n\text{mim}][\text{NTf}_2]$  + toluene;  $n$  is the number of carbon atoms in the alkyl chain of the substituted imidazolium;  $x_{\text{IL}}$  and  $w_{\text{IL}}$  are the mole and weight fraction of ionic liquid, respectively, and  $T$  is the temperature of transition.

$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$
<b><math>n = 2</math></b>								
0.3376	0.6840	302.25	0.3481	0.6940	321.15	0.3513	0.6970	323.65
<b><math>n = 4</math></b>								
0.2591	0.6142	298.51						
<b><math>n = 6</math></b>								
0.1798	0.5155	298.52						
<b><math>n = 8</math></b>								
0.1127	0.3960	317.75	0.1183	0.4090	297.45	0.1217	0.4170	286.65
<b><math>n = 10</math></b>								
0.00192	0.01039	282.75	0.01713	0.08697	339.35	0.02572	0.12607	339.35
0.00493	0.02636	315.75	0.01821	0.09204	340.18*	0.02588	0.12679	339.35
0.00567	0.03024	320.85	0.01826	0.09224	339.65	0.02878	0.13937	339.45
0.00670	0.03554	325.25	0.01878	0.09470	339.75	0.02955	0.14265	338.75
0.00805	0.04246	329.55	0.01883	0.09493	339.75	0.03351	0.15929	339.05
0.00911	0.04783	332.65	0.01924	0.09682	339.55	0.03572	0.16834	340.73*
0.01007	0.05266	335.55	0.02017	0.10110	340.05	0.03967	0.18417	338.35
0.01079	0.05625	335.65	0.02065	0.10332	340.15	0.03996	0.18531	338.30
0.01100	0.05730	337.65	0.02139	0.10670	339.55	0.04315	0.19771	336.25
0.01197	0.06210	338.75	0.02298	0.11389	339.65	0.04956	0.22178	334.15
0.01382	0.07114	339.55	0.02342	0.11585	338.95	0.06314	0.26915	317.55
0.01409	0.07246	339.85	0.02359	0.11665	339.65	0.07582	0.30954	295.55
0.01523	0.07792	339.25	0.02375	0.11736	341.15*	0.08282	0.33041	276.65
0.01667	0.08478	340.25	0.02442	0.12032	339.25			

\* values obtained from linear extrapolation of  $T = f(p)$  to a nominal pressure of 0.1 MPa.

**Table S3** Liquid-liquid phase equilibria data of  $[C_n\text{mim}][\text{NTf}_2]$  +  $\alpha$ -methylstyrene;  $n$  is the number of carbon atoms in the alkyl chain of the substituted imidazolium;  $x_{\text{IL}}$  and  $w_{\text{IL}}$  are the mole and weight fraction of ionic liquid, respectively, and  $T$  is the temperature of transition.

$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$T / \text{K}$
<b><math>n = 2</math></b>								
0.44776	0.72861	264.93	0.47126	0.74691	326.77	0.48691	0.75859	370.68
0.47126	0.74691	326.77	0.47402	0.74900	330.65	0.50107	0.76881	412.77
<b><math>n = 4</math></b>								
0.31521	0.62025	274.59	0.34468	0.65113	325.87	0.36426	0.67031	453.83
0.32295	0.62861	287.36						
<b><math>n = 6</math></b>								
0.00392	0.01468	411.14	0.20867	0.49958	454.40	0.22246	0.51996	297.95
<b><math>n = 8</math></b>								
0.00598	0.02364	364.68	0.04119	0.14735	428.81	0.11119	0.33479	398.42
0.01302	0.05040	406.08	0.05780	0.19795	428.34	0.12848	0.37229	369.73
0.02055	0.07783	420.13	0.08091	0.26153	424.19	0.14882	0.41294	297.29
0.02779	0.10315	426.00	0.09560	0.29839	414.91			
<b><math>n = 10</math></b>								
0.00378	0.01590	299.99	0.02674	0.10479	342.86	0.04604	0.17056	341.26
0.00515	0.02158	309.41	0.02721	0.10647	342.73*	0.04713	0.17407	340.98
0.00561	0.02348	317.71	0.02824	0.11017	342.95	0.04843	0.17818	340.47
0.00761	0.03162	322.88	0.02926	0.11380	342.75	0.05200	0.18943	340.01
0.00831	0.03445	325.50	0.03264	0.12255	343.19*	0.05220	0.19004	339.39
0.00885	0.03664	327.24	0.03227	0.12439	343.02	0.05531	0.19965	338.79
0.00969	0.04002	328.66	0.03400	0.13041	343.00	0.05871	0.20994	337.55
0.01111	0.04566	332.72	0.03669	0.13961	343.05	0.06560	0.23024	334.23
0.01206	0.04945	334.68	0.03737	0.14193	343.30*	0.06708	0.23452	333.01
0.01344	0.05486	336.46	0.03875	0.14657	342.61	0.07176	0.24778	330.21
0.01617	0.06545	339.43	0.03926	0.14829	343.10	0.07243	0.24964	328.60
0.01854	0.07448	340.52	0.03990	0.15042	342.30	0.07592	0.25927	325.85
0.02011	0.08040	341.08	0.04211	0.15777	342.23	0.08036	0.27130	321.02
0.02137	0.08511	341.49	0.04227	0.15827	342.65	0.08355	0.27976	317.09
0.02244	0.08909	341.76	0.04251	0.15906	342.03	0.08698	0.28870	312.52
0.02411	0.09522	342.47	0.04409	0.16425	342.30	0.09025	0.29710	307.05
0.02591	0.10178	342.95	0.04596	0.17030	341.30	0.09276	0.30343	297.98
0.02622	0.10293	343.11						

\* values obtained from linear extrapolation of  $T = f(p)$  to a nominal pressure of 0.1 MPa.

**Table S4** Pressure effects on the liquid-liquid phase equilibria of  $[C_{10}\text{mim}][\text{NTf}_2]$  + aromatic solvent;  $x_{\text{IL}}$ ,  $w_{\text{IL}}$ ,  $p$ , and  $T$  are the mole and weight fraction of ionic liquid, pressure and temperature of transition, respectively.

$x_{\text{IL}}$	$w_{\text{IL}}$	$p/\text{MPa}$	$T/\text{K}$	$x_{\text{IL}}$	$w_{\text{IL}}$	$p/\text{MPa}$	$T/\text{K}$
$[C_{10}\text{mim}][\text{NTf}_2]$ + benzene							
0.00891	0.05478	0.394	316.02	0.01978	0.11510	0.245	318.28
		1.004	315.80			0.511	318.22
		1.575	315.57			1.010	318.14
		3.065	315.23			2.085	318.02
		3.894	315.07			3.024	317.87
		4.755	314.92			4.464	317.69
0.01187	0.07184	0.311	317.69	0.03239	0.17749	0.500	315.25
		0.939	317.57			1.008	315.08
		2.361	317.29			2.013	314.92
		2.992	317.21			3.054	314.57
		3.558	317.13			3.974	314.41
		4.364	316.98			4.749	314.28
$[C_{10}\text{mim}][\text{NTf}_2]$ + toluene							
0.01821	0.09204	1.004	339.03	0.03572	0.16834	0.496	340.22
		1.994	337.75			1.010	339.62
		2.970	336.51			1.601	338.81
0.02375	0.11736	0.198	341.00			2.412	337.68
		0.966	340.10			3.119	336.85
		1.632	339.18			3.584	336.30
						4.192	335.51
$[C_{10}\text{mim}][\text{NTf}_2]$ + $\alpha$ -methylstyrene							
0.02721	0.10647	0.151	342.74	0.03737	0.14193	0.486	343.12
		0.498	342.57			0.986	342.91
		0.998	342.34			1.487	342.68
		1.463	342.06			2.157	342.37
		1.993	341.84			2.662	342.14
		2.536	341.60			3.100	341.97
		3.023	341.40			3.985	341.58
		3.496	341.21			3.534	341.74
		3.970	341.04			0.486	343.12
		1.519	342.58			0.986	342.91
0.03174	0.12255	1.997	342.33				
		2.530	342.07				
		3.949	341.48				