

## Supplementary Materials

**Table S1.** The specific retention volume,  $V_g^0$ , between the probe and IL at various temperatures for the hypothetical liquids at zero pressure.

Probes	ILs	$V_g^0$				
		303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
<i>n</i> -C <sub>6</sub>	[C <sub>5</sub> Ciim]Br	7.74	5.73	4.17	3.58	2.73
	[C <sub>6</sub> Ciim]Br	9.20	6.32	4.45	3.96	3.15
	[C <sub>7</sub> Ciim]Br	11.5	8.83	6.21	4.48	3.52
	[C <sub>8</sub> Ciim]Br	22.7	15.5	10.9	7.86	6.35
<i>n</i> -C <sub>7</sub>	[C <sub>5</sub> Ciim]Br	23.6	16.0	10.9	7.79	5.78
	[C <sub>6</sub> Ciim]Br	26.4	18.0	12.7	8.83	6.21
	[C <sub>7</sub> Ciim]Br	34.4	24.6	16.5	11.8	8.57
	[C <sub>8</sub> Ciim]Br	61.8	40.8	27.4	19.1	13.8
<i>n</i> -C <sub>8</sub>	[C <sub>5</sub> Ciim]Br	67.0	42.5	27.4	18.2	12.5
	[C <sub>6</sub> Ciim]Br	79.8	52.2	34.3	22.5	15.1
	[C <sub>7</sub> Ciim]Br	94.8	70.8	45.0	29.0	19.6
	[C <sub>8</sub> Ciim]Br	176	106	67.7	44.5	30.2
<i>n</i> -C <sub>9</sub>	[C <sub>5</sub> Ciim]Br	171	103	64.1	41.1	27.2
	[C <sub>6</sub> Ciim]Br	221	136	85.4	54.7	36.7
	[C <sub>7</sub> Ciim]Br	261	158	99.2	64.0	42.5
	[C <sub>8</sub> Ciim]Br	422	250	154	99.5	66.3
<i>n</i> -C <sub>10</sub>	[C <sub>5</sub> Ciim]Br	458	258	154	94.4	60.1
	[C <sub>6</sub> Ciim]Br	582	336	200	122	79.0
	[C <sub>7</sub> Ciim]Br	675	390	228	140	89.6
	[C <sub>8</sub> Ciim]Br	1115	618	365	224	142
<i>n</i> -C <sub>11</sub>	[C <sub>5</sub> Ciim]Br	1166	619	347	202	125
	[C <sub>6</sub> Ciim]Br	1451	783	435	257	159
	[C <sub>7</sub> Ciim]Br	1673	906	506	295	182
	[C <sub>8</sub> Ciim]Br	2819	1481	828	481	294
<i>n</i> -C <sub>12</sub>	[C <sub>5</sub> Ciim]Br	2992	1512	776	438	258
	[C <sub>6</sub> Ciim]Br	3693	1837	966	536	317
	[C <sub>7</sub> Ciim]Br	4113	2094	1096	628	361
	[C <sub>8</sub> Ciim]Br	6924	3469	1843	1032	582
benzene	[C <sub>5</sub> Ciim]Br	280	187	131	93.3	69.2
	[C <sub>6</sub> Ciim]Br	271	183	125	89.6	66.6
	[C <sub>7</sub> Ciim]Br	264	177	122	85.4	64.5
	[C <sub>8</sub> Ciim]Br	259	171	117	83.6	62.4
toluene	[C <sub>5</sub> Ciim]Br	558	357	233	166	117
	[C <sub>6</sub> Ciim]Br	532	344	227	165	114
	[C <sub>7</sub> Ciim]Br	504	331	241	161	111
	[C <sub>8</sub> Ciim]Br	563	360	233	157	109
<i>o</i> -xylene	[C <sub>5</sub> Ciim]Br	1697	1022	619	462	301
	[C <sub>6</sub> Ciim]Br	1648	1016	615	439	293
	[C <sub>7</sub> Ciim]Br	1633	1000	587	437	284
	[C <sub>8</sub> Ciim]Br	1568	981	539	437	279

<i>m</i> -xylene	[C <sub>5</sub> C <sub>iim</sub> ]Br	1045	637	394	303	199
	[C <sub>6</sub> C <sub>iim</sub> ]Br	1066	627	400	290	192
	[C <sub>7</sub> C <sub>iim</sub> ]Br	1303	790	481	304	200
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1263	764	475	306	205
<i>p</i> -xylene	[C <sub>5</sub> C <sub>iim</sub> ]Br	1073	646	402	304	200
	[C <sub>6</sub> C <sub>iim</sub> ]Br	1079	673	431	292	200
	[C <sub>7</sub> C <sub>iim</sub> ]Br	1283	769	469	298	197
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1231	745	463	299	201
ethyl benzene	[C <sub>5</sub> C <sub>iim</sub> ]Br	999	604	388	291	193
	[C <sub>6</sub> C <sub>iim</sub> ]Br	1009	624	396	279	188
	[C <sub>7</sub> C <sub>iim</sub> ]Br	1166	734	449	286	191
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1139	704	441	286	193
<i>n</i> -propyl benzene	[C <sub>5</sub> C <sub>iim</sub> ]Br	1736	1034	620	454	293
	[C <sub>6</sub> C <sub>iim</sub> ]Br	2411	1392	832	513	334
	[C <sub>7</sub> C <sub>iim</sub> ]Br	2292	1327	801	501	322
	[C <sub>8</sub> C <sub>iim</sub> ]Br	2409	1402	840	524	340
<i>n</i> -butyl benzene	[C <sub>5</sub> C <sub>iim</sub> ]Br	3613	2002	1160	815	506
	[C <sub>6</sub> C <sub>iim</sub> ]Br	5364	2949	1652	972	606
	[C <sub>7</sub> C <sub>iim</sub> ]Br	5410	2969	1741	1006	617
	[C <sub>8</sub> C <sub>iim</sub> ]Br	5820	3210	1823	1089	677
cyclohexene	[C <sub>5</sub> C <sub>iim</sub> ]Br	48.3	38.2	26.4	18.7	14.7
	[C <sub>6</sub> C <sub>iim</sub> ]Br	60.6	42.5	30.1	21.8	16.0
	[C <sub>7</sub> C <sub>iim</sub> ]Br	57.8	42.7	30.0	21.9	15.9
	[C <sub>8</sub> C <sub>iim</sub> ]Br	63.5	45.7	32.3	23.5	17.6
octene	[C <sub>5</sub> C <sub>iim</sub> ]Br	66.3	46.4	29.3	19.5	13.9
	[C <sub>6</sub> C <sub>iim</sub> ]Br	88.1	56.8	37.1	24.9	17.4
	[C <sub>7</sub> C <sub>iim</sub> ]Br	105	70.0	44.6	30.4	20.7
	[C <sub>8</sub> C <sub>iim</sub> ]Br	137	88.1	56.0	37.4	26.0
pentanone	[C <sub>5</sub> C <sub>iim</sub> ]Br	569	378	245	164	112
	[C <sub>6</sub> C <sub>iim</sub> ]Br	503	326	213	145	102
	[C <sub>7</sub> C <sub>iim</sub> ]Br	451	301	196	130	89.4
	[C <sub>8</sub> C <sub>iim</sub> ]Br	423	274	178	121	84.5
3-pentanone	[C <sub>5</sub> C <sub>iim</sub> ]Br	565	361	232	156	109
	[C <sub>6</sub> C <sub>iim</sub> ]Br	497	321	208	143	100
	[C <sub>7</sub> C <sub>iim</sub> ]Br	446	294	192	128	87.8
	[C <sub>8</sub> C <sub>iim</sub> ]Br	414	266	174	118	83.3
thiophene	[C <sub>5</sub> C <sub>iim</sub> ]Br	828	527	351	231	160
	[C <sub>6</sub> C <sub>iim</sub> ]Br	713	455	301	205	143
	[C <sub>7</sub> C <sub>iim</sub> ]Br	557	355	237	159	111
	[C <sub>8</sub> C <sub>iim</sub> ]Br	471	298	189	124	81.4
nitromethane	[C <sub>5</sub> C <sub>iim</sub> ]Br	3217	2023	1278	849	574
	[C <sub>6</sub> C <sub>iim</sub> ]Br	2469	1561	1003	678	458
	[C <sub>7</sub> C <sub>iim</sub> ]Br	1742	1117	723	474	325
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1305	866	576	390	271
methanol	[C <sub>5</sub> C <sub>iim</sub> ]Br	3137	1981	1273	844	589
	[C <sub>6</sub> C <sub>iim</sub> ]Br	2668	1649	1082	732	530
	[C <sub>7</sub> C <sub>iim</sub> ]Br	1835	1159	746	495	337

ethanol	[C <sub>8</sub> C <sub>iim</sub> ]Br	1463	960	627	416	288
	[C <sub>5</sub> C <sub>iim</sub> ]Br	3670	2207	1375	902	617
	[C <sub>6</sub> C <sub>iim</sub> ]Br	3205	1942	1205	762	497
propanol	[C <sub>7</sub> C <sub>iim</sub> ]Br	2426	1443	908	576	380
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1994	1267	797	512	343
	[C <sub>5</sub> C <sub>iim</sub> ]Br	7997	4693	2727	1670	1067
	[C <sub>6</sub> C <sub>iim</sub> ]Br	7343	4241	2542	1537	960
isopropanol	[C <sub>7</sub> C <sub>iim</sub> ]Br	5991	3359	1970	1194	760
	[C <sub>8</sub> C <sub>iim</sub> ]Br	4872	2965	1792	1093	707
	[C <sub>5</sub> C <sub>iim</sub> ]Br	3046	1817	1093	684	455
	[C <sub>6</sub> C <sub>iim</sub> ]Br	2828	1670	1021	643	418
butanol	[C <sub>7</sub> C <sub>iim</sub> ]Br	2270	1342	809	503	324
	[C <sub>8</sub> C <sub>iim</sub> ]Br	1930	1189	728	459	300
	[C <sub>5</sub> C <sub>iim</sub> ]Br	18057	10073	5594	3264	2013
	[C <sub>6</sub> C <sub>iim</sub> ]Br	16635	8962	4869	2810	1724
2-butanol	[C <sub>7</sub> C <sub>iim</sub> ]Br	15202	8031	4473	2586	1614
	[C <sub>8</sub> C <sub>iim</sub> ]Br	13002	7410	4162	2421	1492
	[C <sub>5</sub> C <sub>iim</sub> ]Br	6260	3394	1982	1211	766
	[C <sub>6</sub> C <sub>iim</sub> ]Br	5638	3066	1765	1089	704
isobutanol	[C <sub>7</sub> C <sub>iim</sub> ]Br	5059	2824	1617	968	603
	[C <sub>8</sub> C <sub>iim</sub> ]Br	4325	2562	1503	913	570
	[C <sub>5</sub> C <sub>iim</sub> ]Br	12090	6409	3735	2247	1375
	[C <sub>6</sub> C <sub>iim</sub> ]Br	10754	5903	3313	1941	1191
	[C <sub>7</sub> C <sub>iim</sub> ]Br	9465	5187	2957	1734	1064
	[C <sub>8</sub> C <sub>iim</sub> ]Br	8099	4729	2735	1630	1005

Standard uncertainties are as follow:  $u(T) = \pm 0.5 \text{ K}$ ,  $u(V_g^0) = 0.03$ .

**Table S2.** Probe description table.

<b>Chemical name</b>	<b>CASRN</b>	<b>source</b>	<b>initial mole fraction purity</b>	<b>Water content</b>	<b>Final mole fraction purity</b>
[C <sub>5</sub> C <sub>1im</sub> ]Br	343851-31-0	Chengjie Chemical Co.Ltd.	0.98	540 ppm	0.999
[C <sub>6</sub> C <sub>1im</sub> ]Br	85100-78-3	Chengjie Chemical Co.Ltd.	0.98	360 ppm	0.999
[C <sub>7</sub> C <sub>1im</sub> ]Br	343851-32-1	Chengjie Chemical Co.Ltd.	0.98	480 ppm	0.999
[C <sub>8</sub> C <sub>1im</sub> ]Br	61545-99-1	Chengjie Chemical Co.Ltd.	0.98	570 ppm	0.999
<i>n</i> -C <sub>9</sub>	111-84-2	J&K Scientific Ltd.	0.99		
<i>n</i> -C <sub>10</sub>	124-18-5	J&K Scientific Ltd.	0.98		
<i>n</i> -C <sub>11</sub>	1120-21-4	J&K Scientific Ltd.	0.98		
<i>n</i> -C <sub>12</sub>	112-40-3	J&K Scientific Ltd.	0.98		
cyclopentane	287-92-3	J&K Scientific Ltd.	0.99		
cyclohexane	110-82-7	J&K Scientific Ltd.	0.995		
2,2,4-trimethylpentane	540-84-1	J&K Scientific Ltd.	0.99		
benzene	71-43-2	J&K Scientific Ltd.	0.995		
toluene	108-88-3	J&K Scientific Ltd.	0.995		
<i>o</i> -xylene	95-47-6	J&K Scientific Ltd.	0.98		
<i>m</i> -xylene	108-38-3	J&K Scientific Ltd.	0.99		
<i>p</i> -xylene	106-42-3	J&K Scientific Ltd.	0.98		
ethyl benzene	64-04-0	J&K Scientific Ltd.	0.99		
<i>n</i> -propyl benzene	103-65-1	J&K Scientific Ltd.	0.98		

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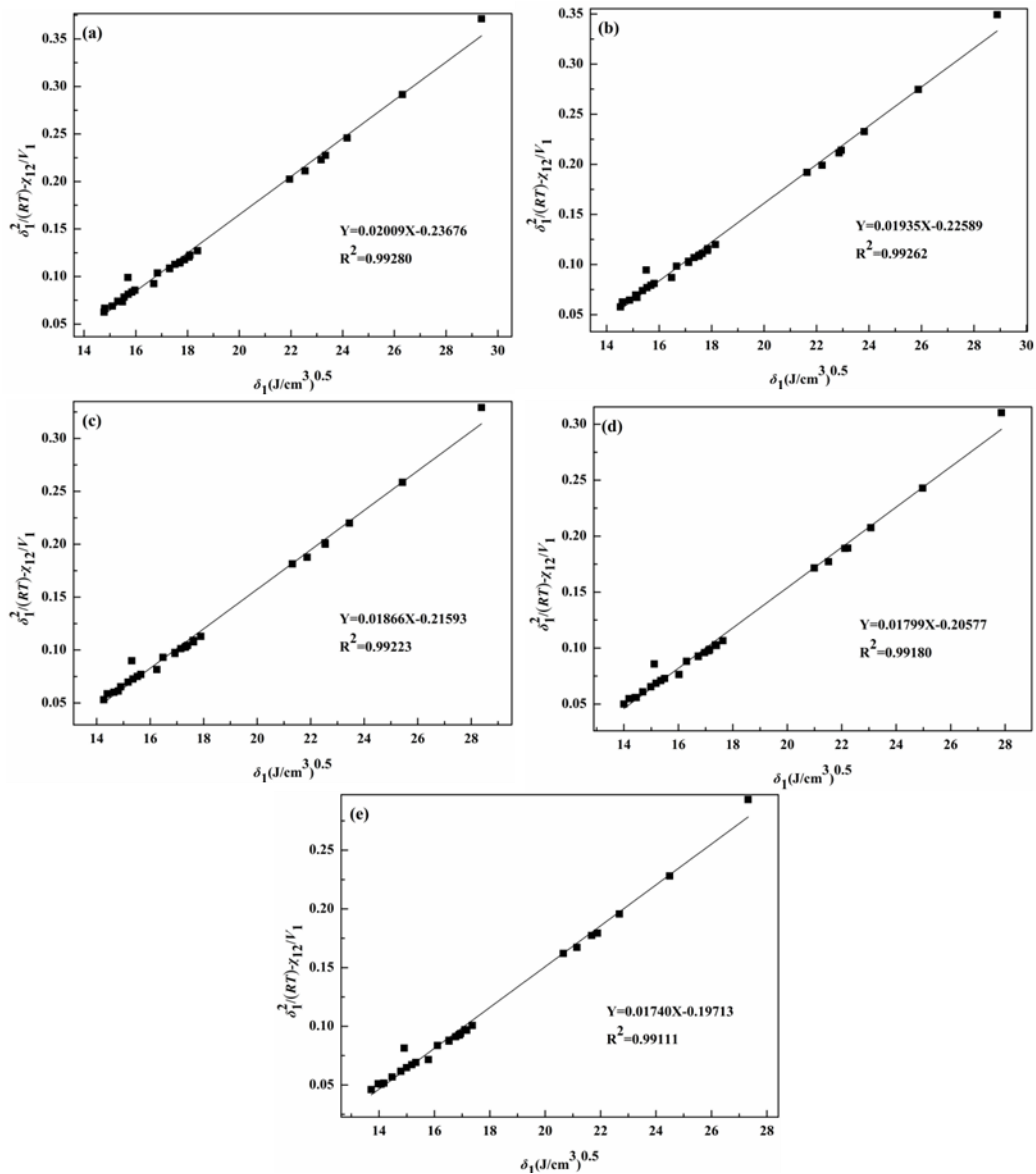
<i>n</i> -butyl benzene	104-51-8	J&K Scientific Ltd.	0.99
acetone	67-64-1	J&K Scientific Ltd.	0.995
nitromethane	75-52-5	J&K Scientific Ltd.	0.995
cyclohexene	110-83-8	J&K Scientific Ltd.	0.99
octene	111-66-0	J&K Scientific Ltd.	0.99
methyl ethyl ketone	78-93-3	J&K Scientific Ltd.	0.99
cyclohexanone	108-94-1	J&K Scientific Ltd.	0.99
dichloromethane	75-09-2	J&K Scientific Ltd.	0.995
chloroform	67-66-3	J&K Scientific Ltd.	0.995
carbon tetrachloride	56-23-5	J&K Scientific Ltd.	0.995
tetrahydrofuran	109-99-9	J&K Scientific Ltd.	0.99
pyridine	110-86-1	J&K Scientific Ltd.	0.99
thiophene	110-02-1	J&K Scientific Ltd.	0.99
propylene oxide	75-56-9	J&K Scientific Ltd.	0.99
1,4-dioxane	123-91-1	J&K Scientific Ltd.	0.99
pentanone	107-87-9	J&K Scientific Ltd.	0.98
3-pentanone	96-22-0	J&K Scientific Ltd.	0.99
methanol	67-56-1	J&K Scientific Ltd.	0.999
ethanol	64-17-5	J&K Scientific Ltd.	0.997

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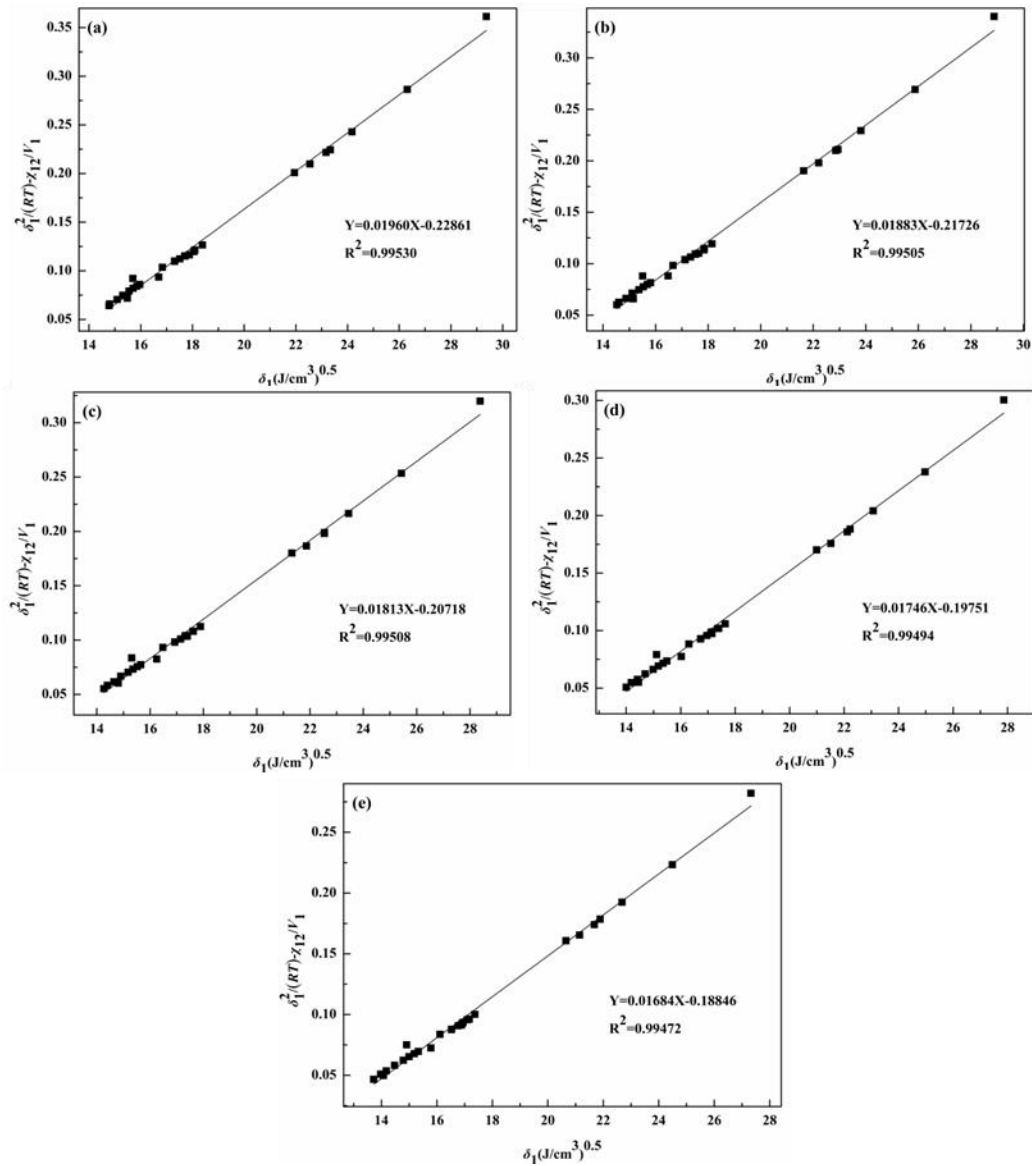
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propanol	71-23-8	J&K Scientific Ltd.	0.995
isopropanol	67-63-0	J&K Scientific Ltd.	0.99
butanol	71-36-3	J&K Scientific Ltd.	0.99
2-butanol	78-92-2	J&K Scientific Ltd.	0.995
isobutanol	78-83-1	J&K Scientific Ltd.	0.99
acetonitrile	75-05-8	J&K Scientific Ltd.	0.99
methyl propionate	554-12-1	J&K Scientific Ltd.	0.99
ethyl propionate	105-37-3	J&K Scientific Ltd.	0.99
methyl formate	107-31-3	J&K Scientific Ltd.	0.99
methyl acetate	79-20-9	J&K Scientific Ltd.	0.98
ethyl acetate	141-78-6	J&K Scientific Ltd.	0.995
<i>n</i> -C <sub>6</sub>	110-54-3	J&K Scientific Ltd.	0.998
<i>n</i> -C <sub>7</sub>	142-82-5	J&K Scientific Ltd.	0.985
<i>n</i> -C <sub>8</sub>	111-65-9	J&K Scientific Ltd.	0.98
<i>n</i> -C <sub>5</sub>	109-66-0	J&K Scientific Ltd.	0.995
ethylene glycol	107-21-1	J&K Scientific Ltd.	0.99
<i>N, N</i> -dimethylformamide	68-12-2	J&K Scientific Ltd.	0.99
dimethyl sulfoxide	2206-27-1	J&K Scientific Ltd.	0.99

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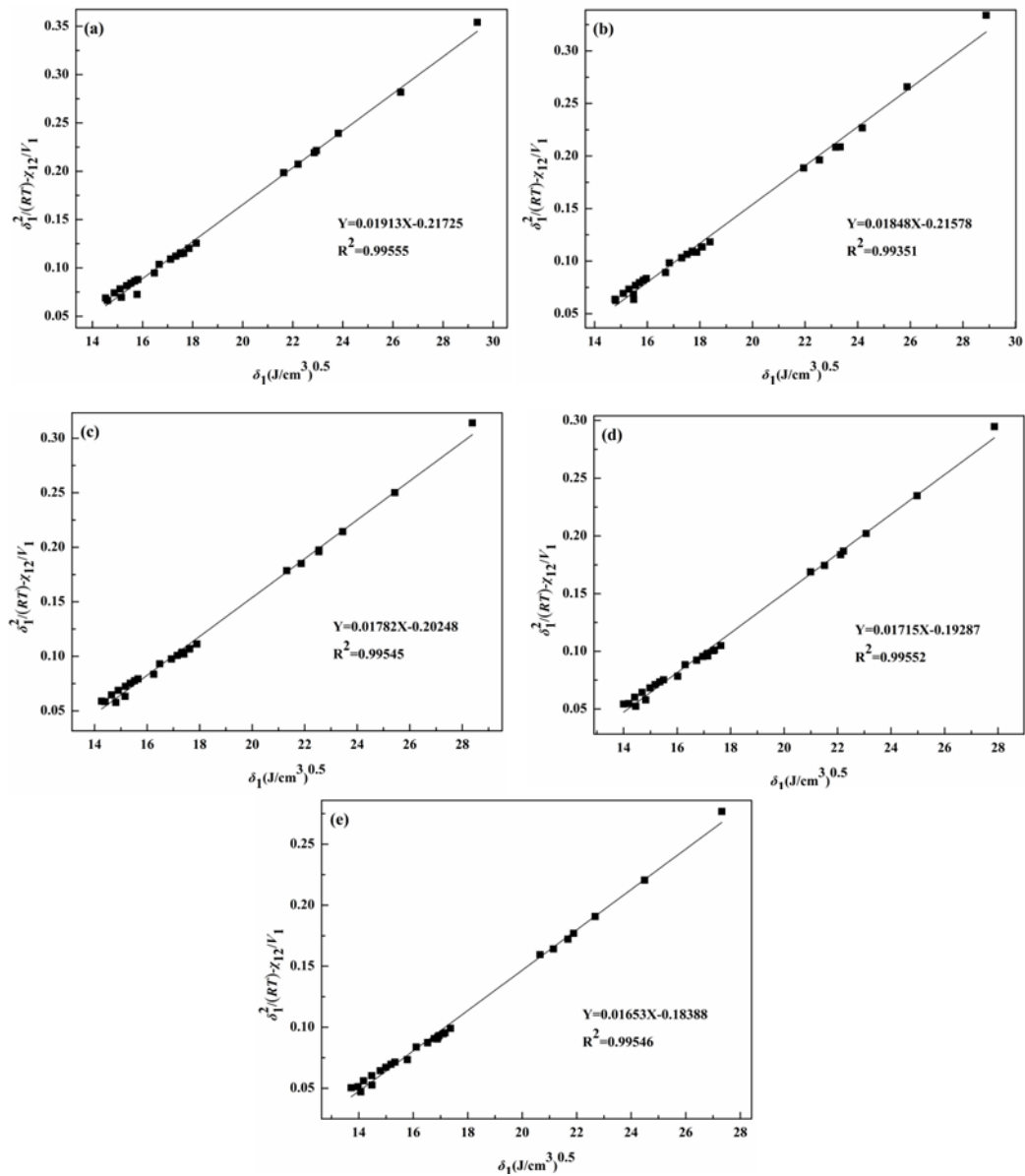


**Figure S1** Variation of the term  $\delta_1^2/RT - \chi_{12}/V_1$  with the solubility parameters of the solvent  $\delta_1$  in [C<sub>6</sub>Crim]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K; (e) at 343.15 K.

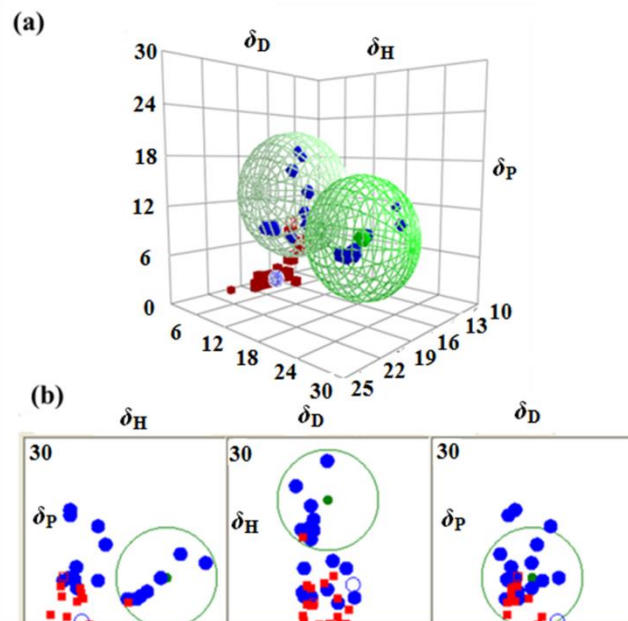


**Figure S2** Variation of the term  $\delta_1^2/RT - \chi_{12}/V_1$  with the solubility parameters of the solvent  $\delta_1$  in [C7C1im]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K.; (e) at 343.15 K.

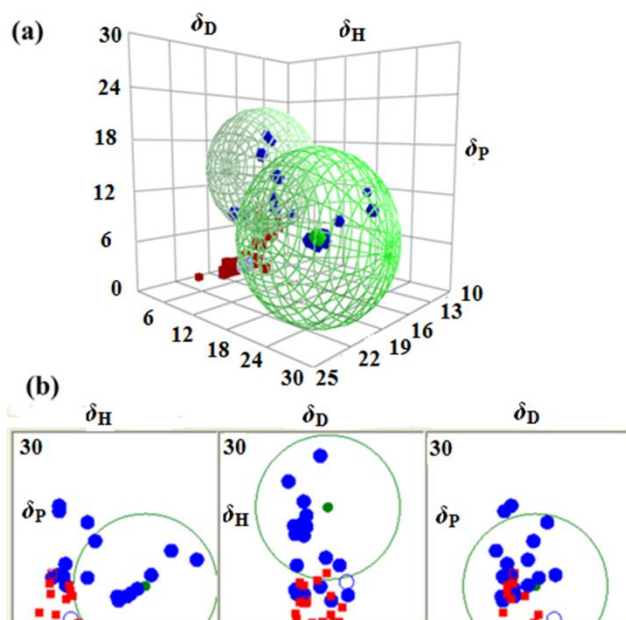




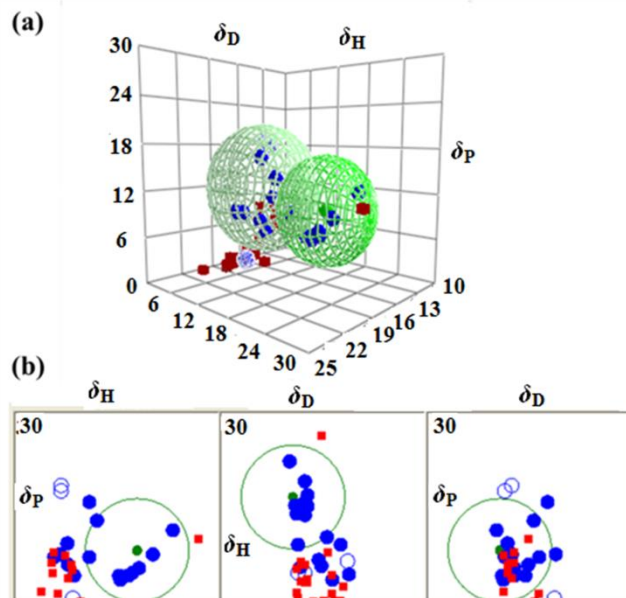
**Figure S3** Variation of the term  $\delta_1^2/RT - \chi_{12}/V_1$  with the solubility parameters of the solvent  $\delta_1$  in [CsC1im]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K.; (e) at 343.15 K.



**Figure S4** (a) The 3D graph with the coordinates of [C<sub>6</sub>Cim]Br; (b) The 2D graphs corresponding to the 3D graph of [C<sub>6</sub>Cim]Br.



**Figure S5** (a)The 3D graph with the coordinates of [C7Cim]Br; (b) The 2D graphs corresponding to the 3D graph of [C7Cim]Br.



**Figure S6** (a) The 3D graph with the coordinates of [CsCiiim]Br; (b) The 2D graphs corresponding to the 3D graph of [CsCiiim]Br.