J. Chem. Thermodynamics 88 (2015) 22–29

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Phase behavior of ionic liquids 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides with halogenated benzenes

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ARTICLE INFO

Article history:
Received 7 August 2014
Received in revised form 21 March 2015
Accepted 8 April 2015
Available online 17 April 2015

Keywords:
Isotope effect
Miscibility
Ionic liquid
(Liquid + liquid) equilibrium
Halogenated benzene

ABSTRACT

(Liquid + liquid) miscibility temperatures as a function of composition have been determined experimentally for the binary systems formed by imidazolium based ionic liquids with bis(trifluoromethylsulfonyl)imide ($[C_nMIM][NTf_2]$: $n = 3$ to 10) with fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and 1,2-dichlorobenzene. In addition, the phase diagrams for deuterated chlorobenzene, bromobenzene and 1,2-dichlorobenzene have been obtained. All the measured systems show the limited miscibility with the upper critical solution temperature behavior. Similarly to the other systems with the imidazolium cation the increase of the alkyl chain length in this cation improves the miscibility. The impact of the halogenobenzene is also very visible. The miscibility is improving in the order: iodobenzene < bromobenzene < chlorobenzene < fluorobenzene. This arrangement corresponds to the decreasing molar volume of the substituted benzenes. The disubstituted chlorobenzene is a better solvent for ionic liquids than chlorobenzene. The replacement of hydrogen for deuterium in halogenobenzenes in all cases improves the miscibility and the isotope shifts of the UCSTs are very large.

1. Introduction

In our previous studies on the phase behavior of the imidazolium based ionic liquids (IL) with bis(trifluoromethylsulfonyl)imide anion with benzene [1] we observed interesting and rather unusual phase behavior. Changing the alkyl side chain in the imidazolium cation it was possible to pass from almost immiscible system through the LCST type phase behavior to "hourglass" configuration and after that reaching finally the typical UCST type phase diagrams. The recent extensive studies [2–4] of the (liquid + liquid) phase equilibria and other thermodynamic properties of 1-ethyl-3-methylimdazolium bis(trifluoromethylsulfonyl)imide ($[C_2MIM][NTf_2]$) with halogenated benzenes also revealed interesting phase behavior. In general, monosubstituted halogenobenzenes [3] show the limited miscibility and immiscibility gap increases in the following order: F < Cl < Br < I. No direct correlation of the miscibility with dipole moments has been found and the authors point for other intermolecular interactions, like higher-order moments, in particular quadrupole moment of the aromatic ring, π-electrons and hydrogen bonding which may play an essential role in controlling the miscibility. On the other hand for di- and multisubstituted fluorobenzenes some correlations with the dipole moment have been suggested although the phase behavior is even more differential – changing from the complete miscibility to almost immiscible system. The full phase diagram was constructed for $[C_2MIM][NTf_2]$ + 1,2,4-trifluorobenzene system only. For other cases only parts of the coexistence curve could be shown, however its curvature suggests that eventual phase diagram could correspond to the LCST behavior. It should also mention here the theoretical study performed by Shimizu *et al.* [5] in the system composing of the same ionic liquid and multisubstituted fluorobenzenes. Basing on their molecular dynamic simulations and appropriate ab initio calculations they were able to show the important role of the multipole moments, in particular the importance of the largest component of the principal-axes quadrupole moment in the solubility behavior of the system studied.

Assuming that the general rule, showing that the miscibility is improving with the increasing length of the side alkyl chain in the imidazolium cation, still holds we decided to extend the miscibility study for other imidazolium cations with alkyl chain ranging from C_2 to C_{10} with various monohalogenated benzenes. These studies will be complemented by the examination of the impact of deuteration in the aromatic solvents on their miscibility with ionic liquids.

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http://dx.doi.org/10.1016/j.jct.2015.04.012
0021-9614/

TABLE 1
Experimental (liquid + liquid) equilibrium mass fractions w, mole fractions x and temperatures T for the systems $[C_xMIM][NTf_2]$[a] or $[C_nMIM][NTf_2]$ (1) + halogenated benzene (2) at pressure p = 0.1 MPa.[b]

$C_{2.37}$[MIM][NTf_2]/C_6H_5**F**			$C_{2.62}$[MIM][NTf_2]/C_6H_5**F**		
w_1	X_1	T/K	w_1	x_1	T/K
		[C_xMIM][NTf_2] (1) + fluorobenzene (2)			
0.2247	0.0651	299.2	0.2233	0.0652	357.2

[C_4MIM][NTf_2]/C_6H_5**Cl**			[C_4MIM][NTf_2]/C_6**D$_5$Cl**			[C_5MIM][NTf_2]/C_6H_5**Cl**		
w_1	X_1	T/K	w_1	x_1	T/K	w_1	x_1	T/K
			[C_nMIM][NTf_2] (1) + chlorobenzene (2)					
0.0959	0.0277	340.0	0.0995	0.0300	325.6	0.0780	0.0215	275.1
0.1025	0.0297	341.0	0.1070	0.0325	326.9	0.0844	0.0234	276.2
0.1089	0.0317	342.3	0.1105	0.0336	327.4	0.0915	0.0255	277.4
0.1163	0.0341	343.0	0.1148	0.0351	328.1	0.0964	0.0270	277.9
0.1230	0.0362	343.7	0.1301	0.0402	329.1	0.1018	0.0286	278.4
0.1344	0.0400	344.3	0.1440	0.0450	329.7	0.1109	0.0314	278.8
0.1448	0.0435	344.9	0.1566	0.0495	330.0	0.1246	0.0357	279.3
0.1581	0.0480	345.3	0.1665	0.0530	330.2	0.1381	0.0399	279.5
0.1711	0.0525	345.5	0.1824	0.0588	330.3	0.1515	0.0443	279.5
0.1859	0.0577	345.7	0.1965	0.0641	330.3	0.1623	0.0479	279.5
0.1967	0.0616	345.7	0.2108	0.0696	329.8	0.1722	0.0512	279.5
0.2089	0.0662	345.5	0.2185	0.0727	329.5	0.1788	0.0535	279.5
0.2192	0.0700	345.0	0.2276	0.0763	328.9	0.1934	0.0586	279.4
0.2273	0.0731	344.6	0.2407	0.0816	328.1	0.2023	0.0618	279.0
0.2392	0.0778	344.0	0.2538	0.0870	326.4	0.2129	0.0656	278.6
0.2578	0.0852	342.9	0.2618	0.0904	325.1	0.2217	0.0689	278.0
0.2755	0.0926	341.4				0.2257	0.0704	277.6
0.2851	0.0966	339.9				0.2312	0.0724	277.1
						0.2412	0.0762	276.3
						0.2447	0.0776	275.8

[C_4MIM][NTf_2]/C_6H_5**Br**			[C_4MIM][NTf_2]/C_6**D$_5$Br**			[C_5MIM][NTf_2]/C_6H_5**Br**		
w_1	X_1	T/K	w_1	x_1	T/K	w_1	x_1	T/K
			[C_nMIM][NTf_2] (1) + bromobenzene (2)					
0.0884	0.0350	389.8	0.0802	0.0326	373.9	0.0682	0.0258	334.3
0.0904	0.0359	390.7	0.0863	0.0352	375.3	0.0744	0.0283	335.0
0.0955	0.0380	391.7	0.0901	0.0368	375.8	0.0805	0.0307	336.0
0.1021	0.0408	392.6	0.0994	0.0409	376.9	0.0872	0.0334	336.6
0.1055	0.0423	392.9	0.1045	0.0431	377.6	0.0921	0.0354	337.1
0.1123	0.0452	393.6	0.1116	0.0463	378.4	0.1005	0.0389	337.7
0.1223	0.0495	394.2	0.1219	0.0509	378.9	0.1115	0.0435	338.1
0.1319	0.0538	394.5	0.1308	0.0549	379.0	0.1229	0.0483	338.3
0.1439	0.0592	394.6	0.1467	0.0622	379.0	0.1369	0.0543	338.3
0.1529	0.0633	394.7	0.1617	0.0693	379.0	0.1558	0.0626	338.3
0.1618	0.0674	394.7	0.1708	0.0737	379.0	0.1699	0.0690	338.1
0.1688	0.0707	394.7	0.1755	0.0759	379.0	0.1878	0.0773	337.5
0.1790	0.0754	394.6	0.1886	0.0824	378.8	0.1961	0.0812	337.0
0.1869	0.0792	394.4	0.2005	0.0883	378.0	0.2095	0.0876	336.1
0.1975	0.0843	394.1	0.2145	0.0954	376.9	0.2162	0.0908	335.4
0.2043	0.0876	393.8	0.2248	0.1007	375.6	0.2231	0.0942	334.1
0.2113	0.0911	393.3	0.2366	0.1069	373.9			
0.2175	0.0942	393.0						
0.2236	0.0973	392.6						
0.2308	0.1009	392.1						
0.2350	0.1031	391.6						
0.2447	0.1081	390.3						
0.2546	0.1133	388.7						

[C_5MIM][NTf_2]/C_6**D$_5$Br**			[C_6MIM][NTf_2]/C_6H_5**Br**		
w_1	X_1	T/K	w_1	x_1	T/K
0.0694	0.0271	316.9	0.0581	0.0212	287.4
0.0727	0.0285	317.6	0.0614	0.0224	288.0
0.0789	0.0310	318.9	0.0685	0.0251	289.0
0.0904	0.0358	319.6	0.0723	0.0266	289.5
0.1056	0.0423	320.3	0.0773	0.0286	290.2
0.1195	0.0483	320.5	0.0863	0.0321	290.9
0.1326	0.0540	320.6	0.0957	0.0358	291.4
0.1454	0.0598	320.5	0.1012	0.0380	291.6
0.1574	0.0652	320.4	0.1113	0.0421	291.8
0.1661	0.0693	320.3	0.1218	0.0464	291.8
0.1765	0.0741	320.1	0.1288	0.0493	291.8
0.1845	0.0780	319.6	0.1339	0.0515	291.7
0.1951	0.0831	318.7	0.1450	0.0561	291.6

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