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Electronic Supplementary Information

Condensed phase behaviour of ionic liquid–benzene mixtures: Congruent melting of a [emim][NTf_2]·C_6H_6 inclusion crystal

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Experimental

Materials

1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, [emim][NTf_2], was synthesised at QUILL (The Queen's University Ionic Liquid Laboratories, Belfast) according to methods found elsewhere,[1] where it underwent first-stage purification. The ionic liquid was washed several times with water to decrease the chloride content. It was confirmed that no precipitation (of AgCl) occurred by adding $AgNO_3$ to the wash water. NMR analyses showed no major impurities in the untreated, original sample, except for the presence of water. Samples of [emim][NTf_2] were further thoroughly degassed, dried, and freed from any small traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperatures (60-80 ºC) for typically 48 h. Then, both the water and chloride contents were analysed. Karl-Fischer titrations revealed very low levels of water (70 ppm) for the treated ionic liquid, as compared with a value of 3900 ppm of water for the untreated sample. The Cl^- specific electrode using the standard addition method has shown a chloride content of 30 ppm. For the determination of the phase diagram - either by the visual method or the DSC - fresh samples of the ionic liquids kept under vacuum were always used immediately prior to the measurements. Benzene (99.5% for analysis ACS-ISO) was purchased from Panreac. Benzene samples were further dried with 3Å molecular sieves. [emim][NTf_2] + benzene mixtures were gravimetrically prepared and the error in the weight fraction composition is estimated to be within $\pm 2 \times 10^{-5}$.

Phase transition determinations

Visual method

The solid-liquid equilibrium temperatures at 0.1 MPa nominal pressure were determined using a dynamic method described in detail previously [2]. The appropriate mixtures of the ionic liquid and benzene were placed in a Pyrex glass cell and inserted in a thermostatic bath filled with a mixture of ethanol and liquid nitrogen. After solidification, the samples were heated very slowly (less than 2 $K \cdot h^{-1}$ near the equilibrium temperature) with continuous

stirring inside the cell until melting occurred. The temperature at which the last crystal disappeared was taken as the temperature of the solid-liquid equilibrium. The crystal disappearance temperatures, detected visually (naked eye determination) were measured using a 4-wire platinum resistance thermometer coupled to a Keithley 199 System DMM/Scanner. The thermometer was calibrated against high accuracy mercury thermometers (±0.01 K). The temperature's accuracy is ±0.05 K and that of the mole fraction did not exceed ±0.0005. The overall uncertainty of the transition temperature measurements, resulting from the visual observation of the disappearance of the last crystals is obviously greater than the instrumental error and is estimated to be ± 1 K.

Crystalographic Information

(See CIF file)

References:

1. P. Bonhôte, A.-P. Dias. M. Armand, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* 1996, **35**, 1168-1178.
2. U. Domańska, *Fluid Phase Equilib.*, 1986, **26**, 201-220.

RESULTS

Differential Scanning Calorimetry

The runs (Fig. S1) were performed in a 2920 MDSC system from TA Instruments Inc. using about 5-12 mg of sample and a heating ramp of 0.01 K/s between 240 and 290 K.

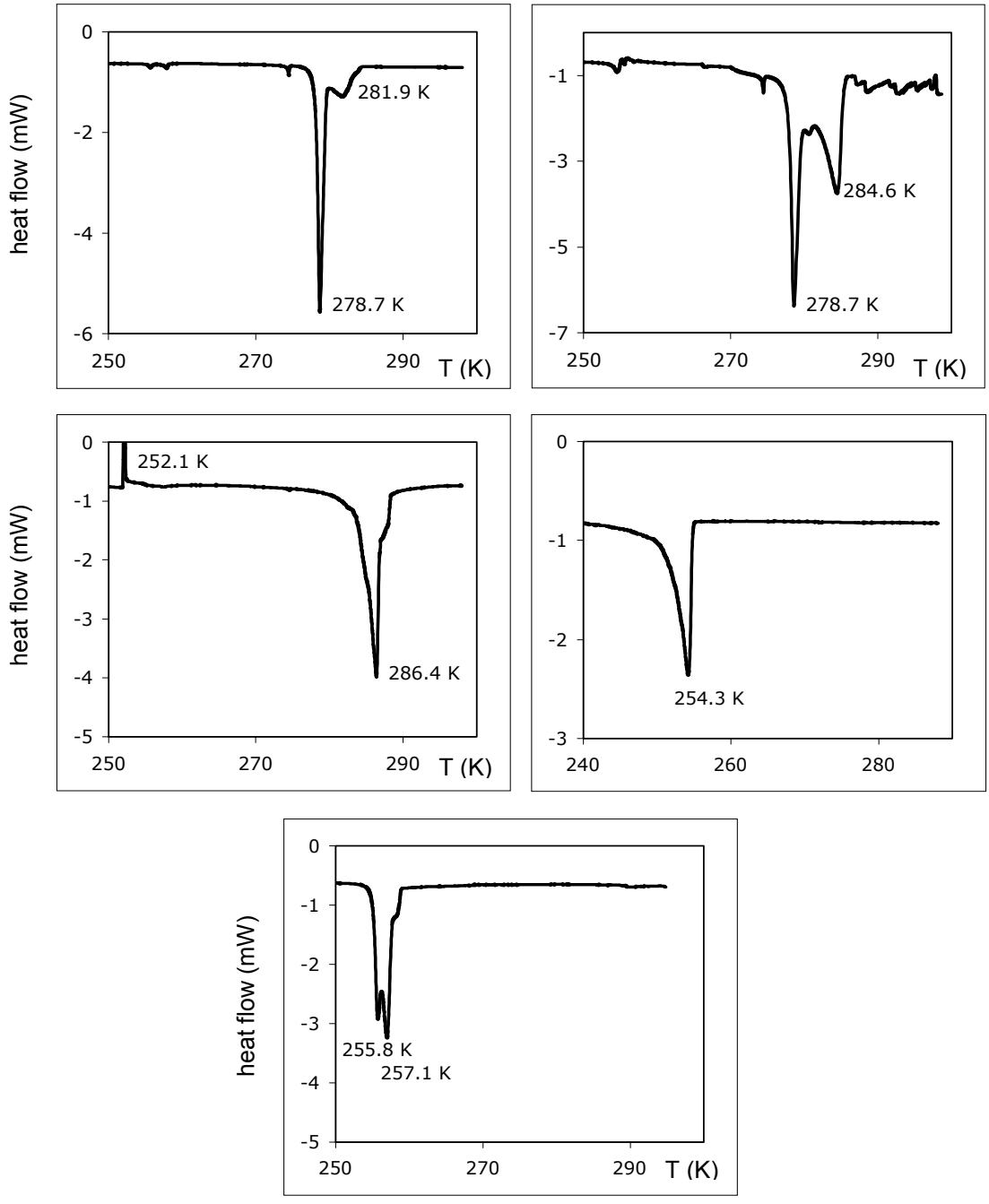

Figure S1 Differential Scanning Calorimetry thermograms of ([emim][NTf_2] + C_6H_6) mixtures: (a) 0.24 x_{IL} ; (b) 0.33 x_{IL} ; (c) 0.45 x_{IL} ; (d) 0.50 x_{IL} ; (e) 0.88 x_{IL}. The sharp positive peak shown in graph (c) corresponds to the crystallization of the inclusion compound upon melting of the metastable solid phase during the heating ramp. Graphs (d) and (e) show only the melting of the metastable solid phase (no inclusion crystal was formed).

Transition temperature data

TABLE S1. Experimental data (visual and DSC) of solid-liquid and liquid-liquid equilibria for 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, [emim][NTf_2], + benzene.

x_{IL}	w_{IL}	T / K	x_{IL}	w_{IL}	T / K	x_{IL}	w_{IL}	T / K
0.0000	0.0000	279.6	0.3103	0.6927	270.2 [b]	0.4591	0.8096	287.1
0.0313	0.1393	279.7	0.3115	0.6939	283.4	0.4656	0.8136	287.3
0.0824	0.3102	279.6	0.3115	0.6939	273.7 [b]	0.4760	0.8198	287.6
0.0998	0.3570	280.2	0.3194	0.7016	284.6 [a]	0.4859	0.8256	287.7
0.1163	0.3972	279.5	0.3194	0.7016	278.7 [a]	0.4909	0.8285	288.0
0.1393	0.4477	279.6	0.3247	0.7066	269.0 [b]	0.4991	0.8331	254.3 [a,b]
0.1402	0.4496	279.5	0.3250	0.7069	270.3 [b]	0.5085	0.8382	288.3
0.1513	0.4718	279.5	0.3326	0.7140	284.2	0.5260	0.8475	253.1 [b]
0.1688	0.5043	279.2	0.3380	0.7190	268.4 [b]	0.5260	0.8475	288.1
0.1795	0.5228	279.4	0.3394	0.7201	284.6	0.5519	0.8605	287.8
0.1909	0.5418	279.1	0.3401	0.7208	266.6 [b]	0.5612	0.8650	287.5
0.2013	0.5580	279.1	0.3497	0.7293	266.8 [b]	0.5793	0.8734	286.8
0.2141	0.5771	279.2	0.3533	0.7324	264.7 [b]	0.6074	0.8857	286.8
0.2142	0.5773	278.5	0.3543	0.7332	285.2	0.6126	0.8879	286.3
0.2222	0.5887	278.9	0.3576	0.7361	284.9	0.6195	0.8908	286.4
0.2222	0.5887	293.0 [c]	0.3596	0.7377	268.3 [b]	0.6429	0.9002	250.7 [b]
0.2234	0.5903	280.0	0.3671	0.7440	264.0 [b]	0.6533	0.9042	286.0
0.2264	0.5945	278.6 [b]	0.3691	0.7456	263.0 [b]	0.6618	0.9074	285.9
0.2264	0.5945	301.9 [c]	0.3755	0.7508	266.6 [b]	0.6912	0.9181	285.1
0.2270	0.5953	277.6 [b]	0.3800	0.7544	285.5	0.7246	0.9295	253.8 [b]
0.2334	0.6039	278.4 [b]	0.3860	0.7590	262.9 [b]	0.7383	0.9339	283.5
0.2343	0.6052	281.0	0.3943	0.7653	264.6 [b]	0.7658	0.9425	282.5
0.2343	0.6052	278.8	0.3943	0.7653	285.8	0.7896	0.9495	281.4
0.2350	0.6061	279.8	0.3944	0.7654	286.0	0.7919	0.9502	281.2
0.2411	0.6141	281.8 [a]	0.3958	0.7664	264.6 [b]	0.8052	0.9539	254.9 [b]
0.2411	0.6141	278.7 [a]	0.4033	0.7720	261.2 [b]	0.8275	0.9601	279.4
0.2461	0.6205	281.0	0.4098	0.7767	286.3	0.8447	0.9646	278.2
0.2469	0.6216	282.2	0.4137	0.7795	261.9 [b]	0.8466	0.9651	256.4 [b]
0.2493	0.6245	276.5 [b]	0.4175	0.7821	286.8	0.8740	0.9720	275.6
0.2601	0.6378	281.3	0.4211	0.7847	258.0 [b]	0.8819	0.9740	255.1 [a,b]
0.2610	0.6389	281.9	0.4265	0.7884	286.8	0.8819	0.9740	257.0 [a,b]
0.2629	0.6411	275.4 [b]	0.4353	0.7943	286.7	0.9100	0.9806	270.4
0.2747	0.6549	282.0	0.4356	0.7945	286.8	0.9166	0.9822	269.2
0.2776	0.6582	282.3	0.4448	0.8005	287.0	0.9518	0.9900	262.7
0.2789	0.6595	273.8 [b]	0.4527	0.8056	286.4 [a]	0.9565	0.9910	260.9
0.2920	0.6738	282.7	0.4527	0.8056	252.0 [a, b]	1.0000	1.0000	258.5
0.2951	0.6771	272.0 [b]	0.4553	0.8072	287.3			

[a] DSC, [b] meta-stable phase diagram, [c] LLE