Condensed phase behaviour of ionic liquid–benzene mixtures: congruent melting of a [emim][NTf$_2$]·C$_6$H$_6$ inclusion crystal†

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The solid–liquid phase diagram of the (1-ethyl-3-methylimida-zolium bis{(trifluoromethyl) sulfonyl} amide + benzene) system was determined and allowed us to identify and characterize an equimolar inclusion compound, [emim][NTf$_2$]·C$_6$H$_6$, with a congruent melting temperature: this type of behaviour, reported here for the first time, together with the X-ray structure of the inclusion compound lays emphasis upon the interactions that are responsible for the existence of liquid clathrates at higher benzene concentrations.

The issue of liquid clathrate formation in (ionic liquid + aromatic compound) mixtures was recently addressed in this journal and elsewhere by Holbrey *et al.* and Deetfelts *et al.*[1,2] In those studies, a range of ionic liquids were shown to interact with benzene, toluene, and xylenes forming well organized phases *viz.* clathrate-type structures in the liquid phase, a phenomenon originally recognised by Surette *et al.*[3] In the specific case of mixtures containing benzene and the ionic liquid dimethylimidazolium hexafluorophosphate, [dmim][PF$_6$], the structures in the crystalline and liquid phases were inferred from X-ray and neutron diffraction results, respectively.[1,2] In a previous work,[4] we showed that benzene and other arenes are quite soluble in, but not completely miscible with [C$_n$mim][NTf$_2$] for alkyl chain lengths, *n*, lower than 10, but becoming completely soluble at room temperature for *n* > 10. In the cases of short alkyl chains in the imidazolium ring (*n* < 6), the resulting immiscibility limits correspond to certain fixed, temperature-independent composition ratios of ionic liquid to arene.

An alternative way to investigate the possibility of liquid clathrate formation in these systems uses the construction of solid–liquid phase diagrams. Here, the existence of inclusion crystals or liquid clathrates should be supported by anomalies in the trends of the melting curves.

In this work, we report on the phase diagram of mixtures of benzene with the ionic liquid 1-ethyl-3-methylimidazolium bistris-flamide, [emim][NTf$_2$]. The rationale for the selection of this particular ionic liquid were two-fold: (i) its low melting point (approximately −15 °C) which facilitates experimental work, and (ii) the fact that a temperature-independent molar ratio of *ca.* 3 : 1 (benzene to ionic liquid) had been reported for the solubility limit of benzene in this ionic liquid.[4] The latter fact pointed out the

possible formation of liquid clathrates or inclusion compounds at this or some other particular composition.

The phase diagram (Fig. 1) was built using solid–liquid and liquid–liquid equilibrium temperature data obtained using a dynamic method with visual detection of the phase transitions. The experimental procedure is discussed in detail in the ESI.† Temperature was measured with a 4-wire platinum resistance thermometer coupled to a 199 System DMM/Keithley multimeter, previously calibrated against high accuracy mercury thermometers, with an accuracy of ±0.01 K. The overall uncertainty—taking into account the dynamic and visual nature of the method—is estimated to be ±1 K. The mixtures were prepared by standard gravimetry with an estimated uncertainty in composition (weight fraction) no greater than ±2 × 10^{-5}.

Differential scanning calorimetry (DSC) runs were also performed at five selected mixtures. These results both confirmed the visual method data and allowed for the calculation of the enthalpy changes. All DSC experiments were performed in a TA Instruments 2920 series calorimeter with temperature ramps of 0.01 K s^{-1} between 250 and 290 K. The temperature–composition
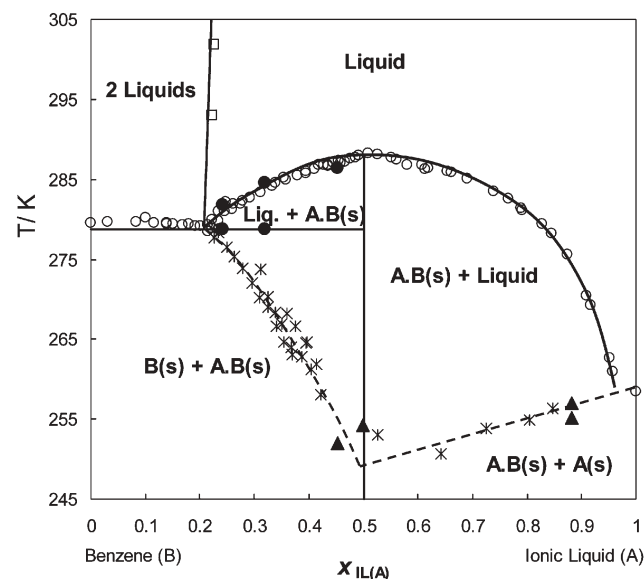
Fig. 1 Phase diagram of the binary mixture [emim][NTf$_2$] (A) + benzene (B). The full lines correspond to solid–liquid equilibria when the inclusion crystal A·B is present—visual cell data (○), DSC data (●); and to liquid–liquid equilibrium data—visual cell data (□). The dashed lines refer to meta-stable situations in which the inclusion crystal is absent due to rapid quenching or deficient mixing of the mixture—visual cell data (*), DSC data (▲).

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data obtained by DSC are included in the phase diagram of Fig. 1 and also given in Table S1 of the ESI;† the DSC runs are illustrated in Fig. S1–S5.†

The most conspicuous and original feature of the diagram, apart from the liquid–liquid immiscibility window ending at the previously reported[4] mole ratio of 3 : 1 (benzene to ionic liquid), is the existence of a congruently melting compound at the equimolar composition, whose melting temperature of +15 ± 1 °C is well above those of both benzene (+5.5 °C)[5] and [emim][NTf$_2$] (−15 ± 1 °C, from this work).‡ To our knowledge this type of behaviour has never been reported for ionic liquid-containing mixtures. The compound is an inclusion crystal with a 1 : 1 molar ratio of benzene to ionic liquid, whose structure was determined by X-ray diffraction (see Fig. 2).§

The DSC results successfully confirmed the visual determinations and provided the following value for the enthalpy of melting of [emim][NTf$_2$]·C$_6$H$_6$: ΔH_m = 42 ± 2 kJ mol^{-1}; to be compared with 24.8 kJ mol^{-1} for [emim][NTf$_2$][11] and 9.3 to 9.9 kJ mol^{-1} for benzene.[5]

Several interesting conclusions can be drawn from the analysis of the X-ray structure and its comparison with the previously published[1] structure for the [dmim][PF$_6$]·0.5C$_6$H$_6$ inclusion compound:

(i) The interactions (contact pairs) between the [NTf$_2$]$^-$ anion and the benzene molecule occur mainly between the hydrogen atoms of the latter and the oxygen atoms of the sulfonate groups of the former—d[C11-H11A…O2] = 3.504 Å (d[H11A…O2] = 2.581 Å, a[C11-H11A…O2] = 171.4°), d[C14-H14A…O4] = 3.339 Å (d[H14A…O4] = 2.495 Å, a[C14-H11A…O2] = 151.1°). Interactions with the fluorine atoms of the [NTf$_2$]$^-$ anion are also present at a lesser extent (see crystal data§). As in the case of [dmim][PF$_6$], the anions cluster around the benzene molecule mainly in the plane of the aromatic ring and the interactions occur in that same plane (see Fig. 5c and d of ref. 2 and Fig. 3 of this work);

(ii) The interactions between the imidazolium cations and benzene are mainly π–π interactions between aromatic rings or interactions between the acidic hydrogens in the cation and the π electrons of benzene, i.e. the cations occupy positions above and
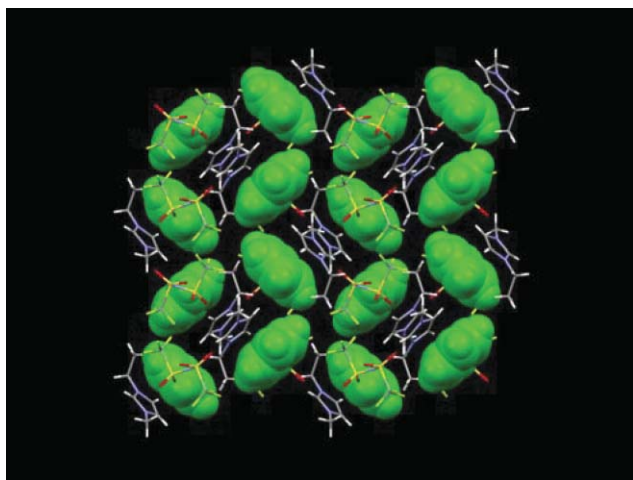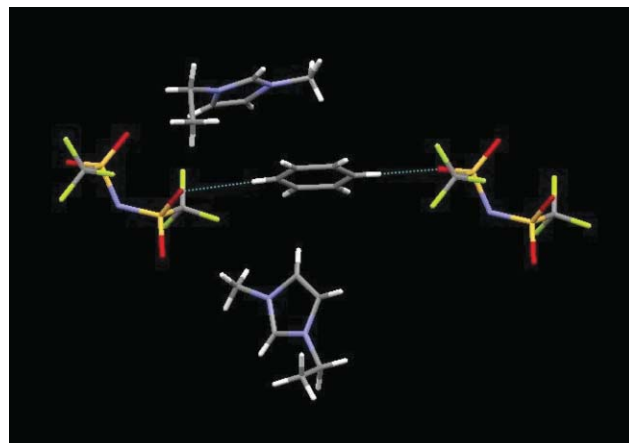
Fig. 3 Representation of the nearest neighbours of a benzene molecule in the [emim][NTf$_2$]·C$_6$H$_6$ inclusion crystal, showing the ionic liquid anions in the plane of the aromatic ring and the cations below and above it both in quasi-coplanar and perpendicular orientations. Dotted lines depict short contacts between the anion's oxygen atoms and the benzene hydrogen atoms (see text).

below the plane of the benzene aromatic ring. This feature is also present in [dmim][PF$_6$]·0.5C$_6$H$_6$ (see Fig. 5a and b of ref. 2). However, in the case of [emim][NTf$_2$]·C$_6$H$_6$, a different layout is found (see Fig. 2 and 3): in contrast to the [dmim][PF$_6$]·0.5C$_6$H$_6$ crystal, the aromatic planes of benzene and the dialkylimidazolium cation are not stacked in piles of parallel arrangements; rather, they exhibit two orientations quasi-perpendicular to each other (cf. Fig. 2 of ref. 1 with Fig. 3).

(iii) Although the general pattern of interactions is similar in the 1 : 2 benzene : [dmim][PF$_6$][1] and 1 : 1 benzene : [emim][NTf$_2$] crystals, the overall structure is quite distinct and reflects the difference in the molar ratios of benzene to ionic liquid. In the [dmim][PF$_6$]·0.5C$_6$H$_6$ crystal, the benzene molecules occupy channels within the structure of the ionic liquid (Fig. 2 of ref. 1). In [emim][NTf$_6$]·C$_6$H$_6$, the structure has to allow for a higher proportion of benzene molecules, forming a tube-like structure with rectangular cross-section around the ionic liquid cations (Fig. 2). As one moves from the 1 : 2 to the 1 : 1 type of inclusion compound the observed trend suggests how cage-like structures of liquid clathrates can assemble at higher proportions of benzene (e.g., 1.5 : 1 or 2 : 1 of benzene to ionic liquid). In other words, from the perspective of the structure of the benzene molecules, the ionic liquid + aromatic system evolves from unidimensional stacks, to tube-like orientations, and, finally, to cage-like arrangements (see schematic in Fig. 4, where the imaginary structure of a hypothetical mixture with 1.5 : 1 of benzene to ionic liquid ratio is compared with the structures of the two known inclusion crystals).

The analysis of the structures of the inclusion compounds can be completed by comparing them with those of the corresponding pure ionic liquids. In the case of [emim][NTf$_2$]·C$_6$H$_6$, this assessment was made with the crystalline structure of pure [dmim][NTf$_2$].[13] In this crystal the main interactions between anions and cations are through the oxygen atoms of [NTf$_2$]$^-$ and the hydrogen atoms of the imidazolium ring or those of the methyl groups. To a lesser extent there are also interactions between the nitrogen and fluorine atoms of [NTf$_2$]$^-$ and the methyl hydrogen atoms of the cation. In the inclusion crystal these types of

Fig. 2 Snapshot of the structure of [emim][NTf$_2$]·C$_6$H$_6$ along the c axis of the monoclinic (P2$_1$/n) crystal, showing the formation of tube-like structures of benzene (depicted in green) around the ionic liquid ions.
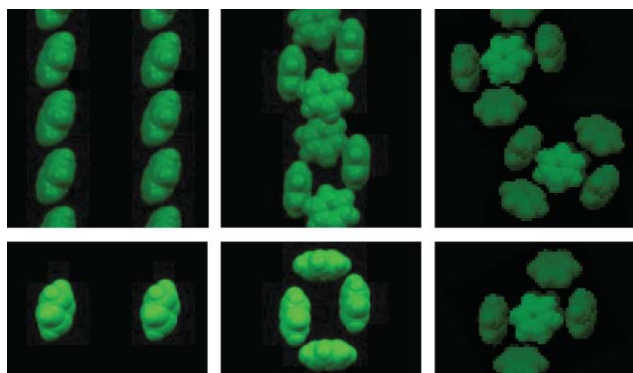
Fig. 4 Schematic representation of the relative position of benzene molecules within the structure of an ionic liquid as its concentration is increased from an ionic liquid·$0.5C_6H_6$ crystal (left) to an ionic liquid·C_6H_6 crystal (center) to a hypothetical ionic liquid·$1.5\ C_6H_6$ clathrate-like structure (right).

interaction between cation and anion are also present, again with predominance for the interactions between the sulfonate oxygen atoms of the anion and the aromatic and methyl hydrogen atoms of the cation. The ionic network is more expanded in the case of the inclusion compound (it has to accommodate for the presence of the benzene molecules) but, nevertheless, it manages to preserve a significant amount of its contact pair interactions. The dual nature of the benzene interactions (equatorial with the anions, polar with the cations) allows the benzene molecules to permeate the ionic structure without disrupting it and justifies the increased stability of the inclusion crystal (*cf.* its higher fusion temperature and molar enthalpy of melting).

In this communication, we show that detailed thermodynamic descriptions of the solid–liquid transition of ionic liquid + benzene mixtures, through the construction of the appropriate phase diagrams, may lead to the discovery and description of inclusion crystals for these systems. Therefore, these investigations are paramount in the search, identification, and characterisation of ionic liquids as liquid clathrate sustaining media.

Notes and references

‡ Other data (literature): +4 °C,[6] −3 °C,[7] −15 °C,[8] −17 °C,[9] −18 °C,[10,11] −21 °C.[12]

§ *Crystal data*: Single crystal X-ray data collection was obtained at the ESRF synchrotron in Grenoble (ID29 beam line) from a crystal of $C_{14}H_{17}F_6N_3O_4S_2$, $M = 469.43$. The crystal belongs to the monoclinic space group, $a = 13.348(3)$ Å, $b = 10.922(3)$ Å, $c = 13.743(3)$ Å, $\beta = 96.753(3)°$, $U = 1989.6$ Å^3, $P2_1/n$ (no.14), $Z = 4$, $T = 110$ K and $\mu = 0.348$ mm^{-1}. The data set comprised 11061 reflections, 2382 unique ($R_{int} = 0.0508$), which were used in all calculations. The hydrogen atoms were positioned as riding atoms and the refinement converged to $wR(F^2)$ (all data) and $wR(F^2)$ (observed data, $F^2 > 2\sigma$) values of 0.1433 and 0.1373, respectively. CCDC 299700. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602675c

1 J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, O. Sheppard, C. Hardacre and R. D. Rogers, *Chem. Commun.*, 2003, 476.
2 M. Deetlefs, C. Hardacre, M. Nieuwenhuyzen, O. Sheppard and A. K. Soper, *J. Phys. Chem. B*, 2005, **109**, 1593.
3 J. K. D. Surette, L. Green and R. D. Singer, *Chem. Commun.*, 1996, 2753.
4 J. Lachwa, J. Szydlowski, A. Makowska, K. R. Seddon, J. M. S. S. Esperança, H. J. R. Guedes and L. P. N. Rebelo, *Green Chem.*, 2006, **8**, 262.
5 http://webbook.nist.gov/chemystry/.
6 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
7 P. Bonhôte, A. -P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168.
8 H. Ngo, K. LeCompte, L. Hargens and A. B. McEwen, *Thermochim. Acta*, 2000, **357**, 97.
9 C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954.
10 H. Every, A. G. Bishop, M. Forsyth and D. R. MacFarlane, *Electrochim. Acta*, 2000, **45**, 1279.
11 H. Tokuda, K. Hayamizu, K. Ishii, Md. A. B. H. Susan and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 6103.
12 S. V. Dzyuba and R. A. Bartsch, *ChemPhysChem*, 2002, **3**, 161.
13 J. D. Holbrey, W. M. Reichert and R. D. Rogers, *Dalton Trans.*, 2004, 2267.