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Liquid clathrate formation in ionic liquid–aromatic mixtures†

John D. Holbrey,[a] W. Matthew Reichert,[a] Mark Nieuwenhuyzen,[b] Oonagh Sheppard,[b] Christopher Hardacre[bc] and Robin D. Rogers*[a]

[a] Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA. E-mail: rdrogers@bama.ua.edu

[b] Department of Chemistry and QUILL, Queen's University of Belfast, Belfast, Northern Ireland, UK BT9 5AG. E-mail: c.hardacre@qub.ac.uk

[c] QUILL, Queen's University of Belfast, Belfast, Northern Ireland, UK BT9 5AG. E-mail: c.hardacre@qub.ac.uk

1-Alkyl-3-methylimidazolium containing ionic liquids with hexafluorophosphate, bis(trifyl)imide, tetrafluoroborate, and chloride anions form liquid clathrates when mixed with aromatic hydrocarbons; in the system 1,3-dimethylimidazolium hexafluorophosphate–benzene, the aromatic solute could be trapped in the solid state forming a crystalline 2 : 1 inclusion compound.

The observation that benzene and many other aromatic compounds are remarkably soluble in, but rarely completely miscible with ionic liquids (ILs),[1] and the recognition that some IL–aromatic systems support liquid clathrate phase formation,[2] led us to investigate IL–aromatic biphasic mixtures and to consider whether liquid clathrate formation was a general characteristic when ILs are mixed with aromatic hydrocarbons. Of particular interest is a detailed knowledge of composition, properties, and interactions within ILs, with relevance to developing improved descriptors for modeling the partitioning of solutes[3] and to understanding rates of reaction and extraction of products from IL-biphase systems. Examples of which include hydrogenation,[4] Friedel–Crafts alkylation,[5] ring-closing metathesis,[6] and polymerization[7] reactions.

The best known examples of liquid clathrates[8] are semi-ordered liquids containing complex salt hosts and aromatic hydrocarbons. Since the first examples, described by Atwood,[9] between highly reactive air-sensitive alkylaluminum salts and aromatics, an expanded range of organic salts (usually) with halide-containing anions, for example $[AlCl_4]^-$, $[HX_n]X^-$, $[X_3]^-$, and also $[BF_4]^-$ anions,[2,10–13] have been shown to support liquid clathrate formation in contact with aromatic solvents. Applications in coal liquefaction[14] and separations of aromatics from hydrocarbons,[15] have been explored.

Liquid clathrate phases are formed by associative interactions between aromatic molecules and salt ions which separate cation–anion packing interactions to a sufficient degree that localized cage-structures are formed. With too little interaction, the salts are simply completely miscible/or immiscible with the aromatics, whereas, if the ion–ion interactions are too great, then crystallization of the salt occurs. Zaworotko and coworkers[12] suggested that liquid clathrate formation depended primarily on the physical properties of the organic salts, and that an approach to developing further liquid clathrate sustaining systems would be to investigate organic salts with low melting points, that is, *ionic liquids*.

Here we report the observation of air- and water-stable liquid clathrates between aromatic hydrocarbons (benzene, toluene, and xylenes) and common 1-alkyl-3-methylimidazolium salts ($[C_nmim]X$) with hexafluorophosphate, bis(trifyl)imide, tetrafluoroborate and chloride anions. The $[PF_6]^-$ and $[NTf_2]^-$ salts differ from other salts reported in the literature as supporting liquid clathrate phases, in that they are hydrophobic[16] and

contain weakly coordinating, non-reactive anions. In one example, $[C_1mim][PF_6]$–benzene, both a liquid clathrate and a solid state inclusion compound are formed with different salt : organic ratio in the liquid and solid state complexes.

When ILs and excess of aromatic hydrocarbons are mixed, liquid clathrate phases form spontaneously under ambient conditions. The IL-rich phases obtained exhibited typical liquid clathrate characteristics, namely, low viscosity (relative to the initial neat ILs), immiscibility with excess aromatic solvents, and non-stoichiometric, but reproducible, compositions. For each IL–organic system, the phases were mixed and allowed to equilibrate for 24 h, ^{1}H NMR was used to determine the composition of the lower, salt-rich phase,‡ shown in Table 1. IL concentration in the upper, aromatic phase was below the ^{1}H NMR detection limit in all the systems examined.

In all examples, the miscibility with benzene was greatest, and the maximum aromatic content in the lower, salt-rich phase of the liquid clathrate biphase decreased following the order benzene > toluene > xylenes. On addition of aromatic the volume of the IL phase was observed to increase. The volume increase was greatest for benzene. The aromatic content of the liquid clathrate phase is somewhat lower than that found in $[Al_2R_6I]^-$ systems,[10] but largely comparable with the values observed in $[(HX)_nX]^-$ containing liquid clathrates,[12] and with the 0.66 mole fraction solubility of benzene in $[C_4mim][PF_6]$ reported by Blanchard and Brennecke.[1]

For the salts that are crystalline at room temperature ($[C_1mim][PF_6]$, $[C_2mim][PF_6]$ and $[C_4mim]Cl$), heating of the salt above the melting point and contacting with an excess of either benzene or toluene also yielded a biphasic system. Cooling to room temperature resulted in crystallization of the lower phase. The imidazolium salts crystallized from the liquid clathrate solutions as pure salts, characterized by X-ray crystallography, consistent with the result reported by Pickett[13] for $[NBu_4][BF_4]$–toluene mixtures (the closest analog system in

Table 1 Ratio of ionic liquid to organic in the lower, IL-rich phase of the liquid clathrate biphasic systems

Ionic liquid	Benzene	Toluene	Xylene		
			o-	m-	p-
$[C_1mim][PF_6]$	1:2.0[a]	*[b]	*[b]		
$[C_2mim][PF_6]$	*[b]	*[b]			
$[C_2mim][NTf_2]$	1:3.0	1:1.7			
$[C_4mim][PF_6]$	1:2.1	1:0.8	1:0.3	1:0.3	1:0.3
$[C_4mim][NTf_2]$	1:3.5	1:2.3	1:1.9	1:1.3	1:1.4
$[C_4mim][BF_4]$	1:1.2	1:0.2	1:0.1	1:0.2	1:0.2
$[C_4mim]Cl$	*[c]	*[c]			
$[C_6mim][PF_6]$	1:3.5	1:1.6	1:1.1	1:0.9	1:0.9

*Denotes observation of biphase at elevated temperatures, above organic salt melting point. [a] Crystallized as 2 : 1 inclusion compound. [b] Crystallized as pure salt. [c] Crystallized as pure $[C_4mim]Cl$ in the monoclinic polymorph.[17]

the literature), except for [C$_1$mim][PF$_6$]–benzene in which a crystalline, but low melting, inclusion compound containing the salt and benzene in a 2:1 stoichiometry was isolated on cooling the molten 1:2 IL–benzene liquid clathrate.

Neutron scattering data also indicates clathrate formation in the liquid of 1:2 [C$_1$mim][PF$_6$]:benzene, where benzene molecules are surrounded by anion–cation cages with strong interactions of the cation methyl groups with the π-system of the benzene.[18]

It is instructive to compare the two crystal structures of [C$_1$mim][PF$_6$] and [C$_1$mim][PF$_6$]·0.5C$_6$H$_6$.† Packing in the two crystals are shown in Fig. 1. In [C$_1$mim][PF$_6$], the asymmetric unit contains one ion pair. The imidazolium cations form a weakly C–H···π hydrogen bonded zigzag chain motif *via* CH$_3$ and the imidazolium ring π-system along the (0 0 1) direction. The [PF$_6$]$^−$ ions are located between these chains and make closest contacts with the methyl hydrogens. Furthermore, because of the zigzag nature of the imidazolium H-bonded chains, the [PF$_6$]$^−$ anions are also associated with the π-system of the cations.
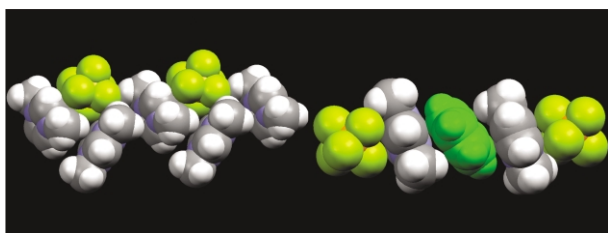

Fig. 1 C–H···π hydrogen-bonded 'zigzag' chain motif of [C$_1$mim][PF$_6$] (left), and cation–benzene 'sandwich' in [C$_1$mim][PF$_6$]·0.5C$_6$H$_6$ (right).

In contrast, in [C$_1$mim][PF$_6$]·0.5C$_6$H$_6$, a three-dimensional array of hydrogen-bonded cations and anions is formed in which the shortest contacts, C(2)–H···F and C(4)–H···F, extend a helical ribbon of cations and anions while C(5)–H···F interactions provide cross-linking between helices. This three dimensional network results in the formation of 'channels' along the (0 0 1) direction of the crystal lattice in which benzene molecules are included (Fig. 2). The benzene molecules do not interact with one another and are isolated within the channels, supported by a staggered π–π 'sandwich' between two imidazolium cations, and bounded by four methyl groups, two from the imidazolium cations of the 'sandwich' and two from neighboring helices, which cause a slight tilting of the ring relative to the adjacent imidazolium cations (Fig. 1, right).

The design principles used for the formation of ILs; low symmetry, organic cations, suppression of melting points by lowering lattice energy, *etc.*,[19] are the same criteria that Zaworotko suggested could be used to increasing the range of
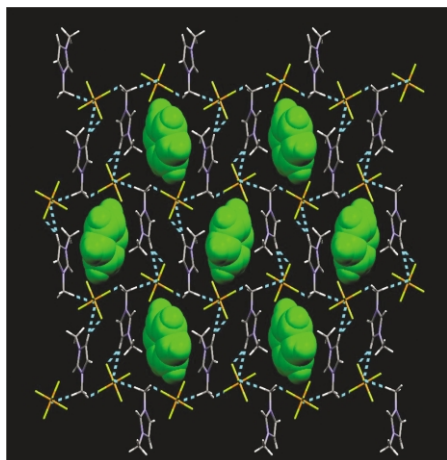
liquid clathrate-supporting salts. The results presented here, for common ILs containing weakly coordinating anions (for example [PF$_6$]$^−$ and [NTf$_2$]$^−$) confirm this and significantly increase the range of salts that support the formation of air-stable liquid clathrates.

Of greatest consequence, the formation of clathrate phases needs to be considered more fully when interpreting the results of reaction or separations processes, or when designing new experiments that utilize an IL–aromatic biphasic system. In addition, it appears likely that further investigation will confirm that ILs, in general, are liquid clathrate sustaining media.

Notes and references

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Fig. 2 Packing in the crystal structure of [C$_1$mim][PF$_6$]·0.5C$_6$H$_6$ showing channels in which the benzene (shown in green) is included.