

# Hydrophobic ionic liquids incorporating *N*-alkylisoquinolinium cations and their utilization in liquid–liquid separations

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Received (in Columbia, USA) 4th September 2001, Accepted 8th October 2001

First published as an Advance Article on the web 6th November 2001

The first examples of Room Temperature Ionic Liquids (RTIL) containing fused polycyclic *N*-alkylisoquinolinium cations ( $[C_n\text{isoq}]^+$ ) in combination with the bis(perfluoroethylsulfonyl)imide anion ( $[\text{BETI}]^-$ ) have been synthesized, characterized, and utilized in liquid–liquid partitioning from water; these salts have unexpectedly low melting points and give high distribution ratios for aromatic solutes, especially chlorobenzenes, between the RTIL and water.

The growth in recent attention given to Room Temperature Ionic Liquids (RTIL) stems from the unique properties inherent to this new class of solvents and their potential to replace volatile organic solvents. RTIL may exhibit miniscule vapor pressure, high thermal stability, unique miscibilities,<sup>1</sup> and a wide temperature range for the liquid phase. In addition, the composite RTIL cations and anions significantly affect the IL miscibility with other solvents (*e.g.*, water), and also the solubility of these solvents in the IL.<sup>2</sup> For aqueous–organic separations, relatively hydrophobic RTIL can be considered as replacements for traditional VOCs while maintaining the basis for biphasic separation.<sup>3–8</sup> Solute partitioning studies indicate that organic solutes have an affinity for the RTIL phase, correlating with their octan-1-ol–water log *P* values,<sup>2,5</sup> or hydrophobicity.

The range of hydrophobic RTIL has, until recently, been limited and largely focused on systems containing imidazolium and pyridinium cations,<sup>9</sup> imidazolium cations have exceptional advantages for electrochemical applications.<sup>10</sup> The number of available RTIL systems has increased due to the incorporation of a large range of different weakly coordinating anions.<sup>11,12</sup> Using perfluorinated anions has led to ionic liquids with attractive properties (hydrophobicity and low viscosity) for applications beyond electrochemistry.<sup>13</sup> Clearly, however, new classes of RTIL are needed, both to further our understanding of RTIL in general and also to find the appropriate combination of physical properties and performance geared towards industrial application.

In this work, a homologous series of *N*-alkylisoquinolinium salts containing linear alkyl substituents from butyl to octadecyl were prepared with the bis(perfluoroethylsulfonyl)imide ( $[\text{BETI}]^-$ ) anion. It was hoped that the extended aromatic system present in these RTIL would lead to specific interactions with other aromatic species that could improve specific separations, *e.g.* in the removal of aromatics from hydrocarbon feedstocks.<sup>1</sup>

The salts were prepared by metathesis from the corresponding chloride salts and were isolated as colorless liquids that separated from aqueous solution. The physical properties for the  $[C_n\text{isoq}][\text{BETI}]$  RTIL are summarized in Table 1. The thermal properties are of particular interest. TGA results show the onset of thermal decomposition begins around 400 °C from where they decompose in the liquid state with a single continuous weight loss with little variation with increasing alkyl chain length. The salts displayed DSC cooling and heating profiles typical for ionic liquids<sup>14</sup> showing a glass transition on cooling and an exothermic transition on heating (corresponding to crystallization) followed by a sharp melting transition of the

Table 1 Characterization of the  $[C_n\text{isoq}][\text{BETI}]$  RTIL<sup>a</sup>

<i>n</i>	Water content (wt%)	Mole fraction water	Melting point ( $T_g/^\circ\text{C}$ )	Glass transition ( $T_g/^\circ\text{C}$ )	Density/ $\text{g cm}^{-3}$
4	1.77	0.36	–62.0	–85.2	1.23
6	1.62	0.35	–77.3	–84.0	1.20
8	1.49	0.35	–68.1	–79.4	1.17
10	0.69	0.20	–59.3	–77.8	1.09
12	0.66	0.20	–51.0	–75.4	1.08
14	0.61	0.20	–49.7	–66.7	1.07
16	0.47	0.16	–48.6	–61.8	1.05
18	0.41	0.15	–47.2	–59.3	1.05

<sup>a</sup> Data measured for RTIL equilibrated against water.

crystalline phase. The variation in glass transitions and melting point with chain length and anion are shown graphically in Fig. 1. Glass transition temperatures generally increase progressively with increasing alkyl-chain length (*n*) owing, perhaps, to the additional energy required to reorient larger cations in the glassy state.

For the series  $[C_n\text{isoq}][\text{BETI}]$ , melting points are affected by the alkyl chain length and decrease from *n* = 4 to 6. This observation may be associated with a possible destabilization of the crystalline state. With further lengthening of the alkyl chain, the melting point increases monotonically, associated with the increasing stability of the crystal state through alkyl–alkyl interactions.

The observed decrease in melting points with increasing alkyl chain length to a minimum for the  $C_6$ -derivatives and then increasing melting point for longer alkyl chain derivatives has been observed as a general feature of organic salts containing an alkyl-chain substituent.<sup>15</sup> The reasons behind this trend are not well understood but it is believed to be a combination of competing factors which influences the stability of the crystal lattice and therefore the melting point; destabilization of cation packing on increasing chain length, and increased chain–chain packing stabilization through microphase separation.

All the  $[C_n\text{isoq}][\text{BETI}]$  RTIL prepared were relatively hydrophobic and separated from water upon metathesis from the  $\text{Li}[\text{BETI}]$  salt as colorless liquids containing around 1%

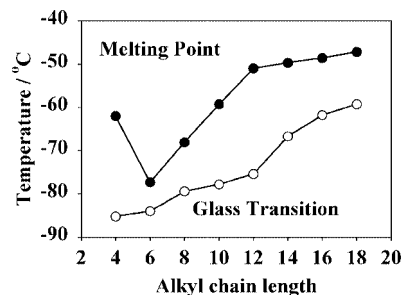
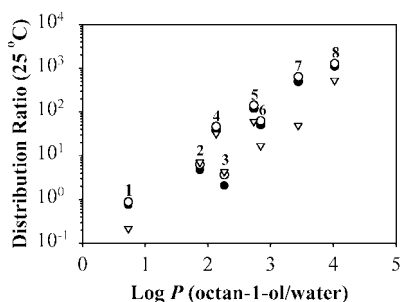


Fig. 1 Glass transition temperatures (○) and melting points (●), for  $[C_n\text{isoq}][\text{BETI}]$  RTIL determined on cooling and heating cycles respectively, by differential scanning calorimetry.



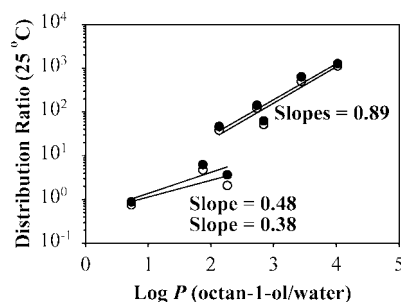
**Fig. 2** Distribution ratios for  $^{14}\text{C}$ -labeled organic solutes (1, phthalic acid; 2, benzoic acid; 3, salicylic acid; 4, benzene; 5, toluene; 6, chlorobenzene; 7, dichlorobenzene; 8, trichlorobenzene) in  $[\text{C}_8\text{isoq}][\text{BETI}]\text{-water}$  ( $\bullet$ ),  $[\text{C}_{14}\text{isoq}][\text{BETI}]\text{-water}$  ( $\circ$ ), or  $[\text{C}_4\text{mim}][\text{PF}_6]\text{-water}$  ( $\nabla$ ) as a function of the solutes' octan-1-ol-water log  $P$  value.

(wt.) of water. The water content of the RTILs corresponds to approximately 0.35–0.15 mole fraction. With increasing chain length, the salts become less dense and increasingly hydrophobic (see Table 1) as the contribution from the alkyl-chain to the liquid structure increases.

The octyl- and tetradecyl-substituted RTIL were used in liquid–liquid separation for a series of aromatic solutes and the results are compared to  $[\text{C}_4\text{mim}][\text{PF}_6]\text{-water}$  systems in Fig. 2. As the solute hydrophobicity increases (as noted by the octan-1-ol–water partition coefficient, log  $P$ ), the general trend is for an increase in the distribution ratios for the organic solutes. Using log  $P$  provides at best only a general parameter for comparing solute partitioning behavior in these systems since, the environment in an ionic liquid is clearly different from that in octan-1-ol. Certain solutes, (*e.g.*, benzoic and salicylic acids) may interact *via* hydrogen bonding and partition as complex species, hence the break in the trend for those solutes.

The data in Table 1 indicate that the  $[\text{C}_{14}\text{isoq}][\text{BETI}]$  RTIL is the most hydrophobic and, in fact, the data in Fig. 2 show a slight increase in the distribution ratios for most hydrophobic solutes in liquid–liquid systems with that RTIL. It is of particular interest to note that the distribution ratios for substituted aromatics with the isoquinolinium systems are higher than with  $[\text{C}_4\text{mim}][\text{PF}_6]$  as the extracting phase.<sup>2</sup> With  $[\text{C}_{14}\text{isoq}][\text{BETI}]$ , the distribution ratio for 1,2,4-trichlorobenzene is 1280 compared to 524 with  $[\text{C}_4\text{mim}][\text{PF}_6]$ .<sup>2</sup> For the series of solutes (*e.g.*, carboxylic acids or substituted aromatics) examined here, the slope of the carboxylic acid partitioning data (0.44) is approximately half that of the aromatic hydrocarbons and halogenated aromatic solutes (0.89), as shown in Fig. 3. It is not yet clear whether the enhanced distribution ratios, particularly for aromatic species, are due to the hydrophobicity in the isoquinolinium RTIL or to increased aromatic interactions.

This series of new, hydrophobic ionic liquids based on the *N*-alkylisoquinolinium<sup>†</sup> cation and the  $[\text{BETI}]^-$  anion has been characterized and the thermal properties of the salts have been described. All the salts are hydrophobic and are liquids at room temperature, prompting the investigation of their use as a component for aqueous-IL two-phase separation systems. The availability of ionic liquids containing a conjugated aromatic core in particular, offers significant potential opportunities for the separation of aromatic compounds from aqueous or hydrocarbon sources.



**Fig. 3** Linear regression of the distribution ratios from Fig. 2 for the sets of acid (lower points 1–3) and aromatic (upper points 4–8) solutes partitioned between  $[\text{C}_8\text{isoq}][\text{BETI}]\text{-water}$  ( $\bullet$ ) or  $[\text{C}_{14}\text{isoq}][\text{BETI}]\text{-water}$  ( $\circ$ ).

This research has been supported by the U. S. Environmental Protection Agency's STAR program through grant number R-82825701-0. Additional support was provided from the PG Research Foundation.

## Notes and references

<sup>†</sup> Chloride salts were prepared by *N*-alkylation of isoquinoline with the respective alkyl chloride. The *N*-alkylisoquinolinium salts were prepared by metathesis in aqueous solution from the respective chloride salts with  $\text{Li}[\text{BETI}]$  (3 M). Distribution ratios are measured as the radioactivity in the lower (RTIL) phase divided by the radioactivity in the upper (aqueous) phase, the standard radiochemical assay utilized is described elsewhere.<sup>2</sup> Water content, melting point, thermal decomposition, and density measurements were performed as described in the literature.<sup>2</sup>

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