

## Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction

Jonathan G. Huddleston, Heather D. Willauer, Richard P. Swatloski, Ann E. Visser and Robin D. Rogers\*†

Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

The partitioning of simple, substituted-benzene derivatives between water and the room temperature ionic liquid, butylmethylimidazolium hexafluorophosphate, is based on the solutes' charged state or relative hydrophobicity; room temperature ionic liquids thus may be suitable candidates for replacement of volatile organic solvents in liquid–liquid extraction processes.

Liquid–liquid extraction has often been a favored choice of the process engineer for the development of separation processes.<sup>1</sup> Traditional solvent extraction,<sup>2</sup> however, employs an organic solvent and an aqueous solution as the two immiscible phases and the increasing emphasis on the adoption of clean manufacturing processes and environmentally benign technologies may make such processes seem increasingly anachronistic because of their high usage of toxic, flammable, volatile organic compounds (VOCs). The costs of solvents are high and their safe engineering attracts significant capital costs over and above simple containment. Disposal of spent extractants and diluents will also attract increasing costs through the impact of environmental protection regulations. So much are VOCs the normal media for organic synthetic processes, that current worldwide usage of these materials has been estimated at over 5 billion dollars per annum.<sup>3</sup>

The design of safe and environmentally benign separation processes has an increasingly important role in the development of clean manufacturing processes and in the remediation of sites contaminated by an older generation of manufacturing technologies. Recently, considerable interest has been manifest in the use of room temperature ionic liquids as solvents for industrial catalytic reactions, including polymerizations, alkylations, and acylations.<sup>3–6</sup> This approach appears to allow the controlled production of desired products from reactants with a minimum of waste production through side reactions due to the tendency of ionic liquids to suppress conventional solvation and solvolysis phenomena.<sup>3,4</sup>

Room temperature ionic liquids are liquids that are composed entirely of ions, and in this sense alone resemble the ionic melts which may be produced by heating normal metallic salts such as sodium chloride to high temperature (*e.g.* NaCl to over 800 °C).<sup>3</sup> In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as –96 °C) and appear to be undemanding and inexpensive to manufacture.<sup>3–5</sup> Ionic liquids based on methylimidazolium are favorable species for investigation because of their air and water stability, their wide liquidus range, the fact that they remain liquid at room temperature, and their relatively favorable viscosity and density characteristics.<sup>7,8</sup> In addition, the R group of the cation is variable and may be used to fine tune the properties of the ionic liquid. It is reported that such ionic liquids are able to solvate a wide range of species including organic, inorganic, and organometallic compounds. Miscibility with a number of organic solvents such as benzene and toluene has also been reported.<sup>9</sup>

In view of these developments, it seems likely that the design and implementation of separation processes for product recovery from these media will assume increasing importance. Additionally, it may be apparent that *ionic liquids may in*

*themselves be suitable, and indeed favorable, media for the design of novel liquid–liquid extraction systems.* Some features of these ionic liquid systems, the high solubilities of organic species, the prevalence of high coulombic forces resulting in the practical absence of any significant vapor pressure,<sup>3</sup> and the availability of air and moisture stable, water immiscible ionic liquids (*e.g.* imidazolium salts of PF<sub>6</sub><sup>–</sup> or BF<sub>4</sub><sup>–</sup>) may recommend such systems as being uniquely suited to the development of completely novel liquid–liquid extraction processes. The data presented here indicate that the partitioning of a number of charged and uncharged aryl organic moieties in a biphasic extraction system comprising the phases butylmethylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]) and water is similar to their partitioning in traditional organic solvent–water systems.

[BMIM][PF<sub>6</sub>] was prepared by modification of published procedures.<sup>‡</sup> Equal volumes of the ionic liquid and distilled deionized water were contacted in the presence of <sup>14</sup>C-labelled tracers of several ionizable and nonionizable substituted aryl molecules. The distribution of the solutes between the heavy, ionic liquid phase and the light, water phase was determined radiochemically.

The distribution data provided in Fig. 1 highlight the relationship between the distribution ratios observed here and similar partitioning in octan-1-ol–water systems (an often used empirical hydrophobicity scale).<sup>10</sup> There is a close relationship between the two systems, although there appear to be differences in detail as is usual in comparing partition between different solvent systems having differing solvation properties.<sup>11,12</sup> The values of the distribution coefficients (*P*) in the octan-1-ol–water system are in general an order of magnitude higher than the corresponding distribution ratios (*D*) for the [BMIM][PF<sub>6</sub>]–water system. The reasons for this have not yet



Fig. 1 Correlation of partitioning data between [BMIM][PF<sub>6</sub>]–water and octan-1-ol–water biphasic systems



**Fig. 2** The solutes studied include: **1** phthalic acid ( $pK_1 = 2.89$ ,  $pK_2 = 5.51$ ), **2** aniline ( $pK_b = 9.42$ ), **3** 4-hydroxybenzoic acid ( $pK_1 = 4.48$ ,  $pK_2 = 9.32$ ), **4** benzoic acid ( $pK_a = 4.19$ ), **5** salicylic acid ( $pK_1 = 2.97$ ,  $pK_2 = 13.40$ ), **6** p-toluic acid ( $pK_1 = 2.27$ )

been elucidated, but may reflect a generally less hydrophobic character to the [BMIM][PF<sub>6</sub>] phase, or may also be due to the strong polar contribution of the relatively high concentration of charged groups present in the ionic liquid compared to the octan-1-ol-water system. These differences do not necessarily imply that ionic liquids represent a 'poorer' extracting phase than octan-1-ol; the distribution values found are adequate for practical applications.<sup>2</sup>

Fig. 1 also shows that for this rather limited set of solute species, those species having charged groups or strong hydrogen bonding moieties (open symbols in Fig. 1) have, in general, much lower partition coefficients than similar neutral or apolar species (filled symbols in Fig. 1). The effect of charge on the distribution of these species was thus investigated further. The ionizable solutes were partitioned in the [BMIM][PF<sub>6</sub>]-water system as described above, but with the pH of the aqueous phase adjusted to either pH 1.77 (using concentrated H<sub>2</sub>SO<sub>4</sub>) or to pH 11 (using concentrated NH<sub>4</sub>OH).

The data in Fig. 2 confirm that the distribution coefficient is higher for the uncharged form than for the charged form. For benzoic acid (**4** in Fig. 2) the partition coefficient is higher under acidic or near neutral conditions than in basic solution. For the oppositely charged base, aniline (**2**), the partition coefficient is higher at alkaline pH than in acidified solution. Similar behavior is observed for the other ionizable solutes employed in the study. It is even possible to rationalize differences in solute partitioning at a given pH from the understanding of the predominant charged state in solution (*i.e.* by comparing the  $pK_a$  values and the predicted magnitude of the molecule's charge at that pH).

It is worth noting that, in almost all cases, the distribution of these solutes varies from values of  $D$  greater than 1 to less than 1 depending on the charged state of the solutes. This indicates a change in phase preference between solutes in their charged and uncharged forms. Once again, this is a useful observation and simplification implying that classical techniques of solvent extraction, which are often ideally designed around the fractionating power which may be achieved by the adoption of forward and backward extracting steps,<sup>1,2</sup> may easily be adapted to extractions performed utilizing ionic liquids.

Ionic liquids represent a novel class of solvents and may now also be considered as a novel medium for liquid-liquid extraction. Limited experience with room temperature ionic liquids based on alkylmethylimidazolium hexafluorophosphate suggests that such systems may be easily adapted to conventional liquid-liquid extraction practice.<sup>¶</sup> The observation of an approximate correspondence between the distribution of these aryl solutes in the ionic liquid system and their distribution in an octan-1-ol-water system is a useful design criterion. Interestingly, the low vapor pressures of such systems suggest novel methods of solute recovery through evaporative-pervaporative techniques for appropriately volatile solutes. These interesting biphasic systems continue to be actively studied in our laboratories for the development of novel, 'clean' separation technologies.

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## Notes and References

† E-mail: RDRogers@Bama.ua.edu

‡ 1-Butyl-3-methylimidazolium chloride was prepared by reaction of equal molar amounts of 1-methylimidazole and chlorobutane in a round-bottomed flask fitted with a reflux condenser by heating and stirring at 70 °C for 48–72 h. The resulting viscous liquid was allowed to cool to room temperature and then was washed three times with 200 mL portions of ethyl acetate. After the last washing, the remaining ethyl acetate was removed by heating to 70 °C under vacuum. To prepare the ionic liquid, hexafluorophosphoric acid (1.3 mol) was added (slowly to prevent the temperature from rising significantly) to a mixture of 1-butyl-3-methylimidazolium chloride (1 mol) in 500 mL of water. After stirring for 12 h, the upper acidic aqueous layer was decanted and the lower ionic liquid portion was washed with water (10 × 500 mL) until the washings were no longer acidic. The ionic liquid was then heated under vacuum at 70 °C to remove any excess water.

§ The procedures used in the standard radiochemical assay utilized are described in ref. 13 for similar work investigating aqueous biphasic systems. Standard radiometric assay of equal volumes of the separated phases allows calculation of the distribution ratio as the ratio of the activity in the ionic liquid phase over the activity in the water phase.

¶ Although we were unable to detect water in the ionic liquid by TGA, NMR does indicate the presence of a small amount of water after contact with an aqueous phase. The exact composition and water content of these potential solvents are under active investigation.

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