

ARTICLES

Ionic Liquids in Separations

XINXIN HAN AND DANIEL W. ARMSTRONG*

Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

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ABSTRACT

Ionic liquids are liquids composed completely of ions. In the past two decades, ionic liquids have been widely used as “green solvents” replacing traditional organic solvents for organic synthesis and catalysis. In addition, ionic liquids are playing an increasingly important role in separation science. In this Account, the application of ionic liquids in all areas of separation science including extractions, gas chromatography, and supported liquid membrane processes are highlighted.

1. Introduction

It has been the traditional view that the melting points of salts are high. For example, sodium chloride melts at 801 °C. However, there is a class of salts or salt mixtures with melting points below 100 °C, which are referred to as ionic liquids (ILs). Room-temperature ionic liquids (RTILs) are ILs with melting points at or below ambient temperature. The cationic parts of most ionic liquids are organic-based moieties such as imidazolium, *N*-alkylpyridinium, tetraalkylammonium, and tetraalkylphosphonium ions. The anionic parts can be organic or inorganic and include such entities as halides, nitrate, acetate, hexafluorophosphate ([PF₆]), tetrafluoroborate ([BF₄]), trifluoromethylsulfonate ([OTf]), and bis(trifluoromethanesulfonyl)imide ([NTf₂]). The most common cations and anions are listed in Figure 1. The first RTIL, ethylammonium nitrate (mp 13–14 °C), was reported in 1914.¹ However, ILs did not draw much attention from chemists till 1992, when Wilkes and co-workers reported air- and water-stable RTILs based on imidazolium salts.² Subsequently, research on the synthesis, properties, and applications of RTILs has increased substantially.

Ionic liquids have unique physicochemical properties. For example, RTILs can have a broad liquid range. Many RTILs remain in a liquid state at temperatures between ~0 and 300 or even 400 °C in the case of more recently

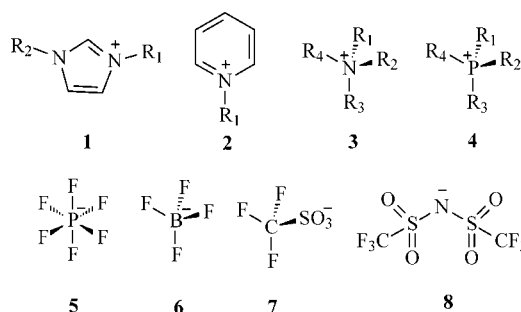


FIGURE 1. Common cations and anions of room-temperature ionic liquids. Cations: **1**, imidazolium ion; **2**, *N*-alkylpyridinium ion; **3**, tetraalkylammonium ion; **4**, tetraalkylphosphonium ion. R_1 , R_2 , R_3 , and R_4 are alkyl groups and can be the same or different. Anions: **5**, hexafluorophosphate ([PF₆]); **6**, tetrafluoroborate ([BF₄]); **7**, trifluoromethylsulfonate ([OTf]); **8**, bis(trifluoromethanesulfonyl)imide ([NTf₂]).

developed ILs.^{3,4} Ionic liquids have low to negligible vapor pressures. However a recent report indicated that several 1-*n*-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides ([C_{*n*}MIM][NTf₂]) could be vacuum distilled at a rate of 0.024–0.12 g/h (at 300 °C and 10⁻⁴ bar).⁵ Many, but not all, ILs show high thermal stability. Some ILs with imidazolium cations and weak nucleophilic anions were stable at 250 °C,⁶ and some dicationic ionic liquids are stable at temperature exceeding 400 °C.⁴ Most ILs are nonflammable; however some with nitrate or perchlorate anions are combustible.⁷ In fact, a special class of ILs referred to as “energetic ionic liquids” are being developed as high explosives.⁷ Ionic liquids may be the most complex of all solvents because they are capable of virtually all possible types of interactions with solutes.⁶ ILs can solubilize a variety of organic and inorganic compounds. They can be designed to be immiscible or miscible with water and a number of organic solvents.

The physicochemical properties of RTILs are influenced by both their cationic and their anionic moieties. For example, both the densities and surface tensions of ILs based on [C_{*n*}MIM] cations with the same anion decrease when the length of alkyl chain increases.⁸ In contrast, the viscosities of the same group of ILs with the same anion increase with an increase in alkyl chain length.⁸ The solubility of ILs depends on both the cation and anion. For example, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and [BMIM][BF₄] are soluble in water, while [BMIM][PF₆] and [BMIM][NTf₂] are immiscible with water.⁶ Increasing the length of alkyl chain on the cation lowers the solubility of ILs with [BF₄] anions. 1-Octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF₄]) is immiscible with water.⁹ Combinations of different possible cations and anions result in a large number of ionic liquids with different properties. Therefore, RTILs often are referred to as “tailor-made or tunable materials”.¹⁰

* E-mail: sec4dwa@uta.edu.

Xinxin Han has received his B.S. (1998) and M.S. (2001) degrees in Nankai University. He is currently a Ph.D. student in Professor Armstrong's group at the University of Texas at Arlington. His research interests include separation of racemates on chiral stationary phases, development of new chiral stationary phases, and application of ionic liquids as GC stationary phases.

Daniel W. Armstrong is the Robert A. Welch professor at the University of Texas at Arlington. He received his B.S. (1972) in Science and Math at Washington and Lee University, M.S. (1974) in Oceanography from Texas A & M University, and Ph.D. (1977) in chemistry from Texas A & M University. Prior to his current position, he was the Caldwell Chair at Iowa State University. His research interests include topics in chiral molecular recognition, colloid science, separation science, ionic liquids, and rapid microbial analysis.

One ionic liquid, *N*-methylimidazolium chloride (mp 75 °C), was employed in an industrial process for the manufacture of alkoxyphenylphosphines on a multiton scale.¹¹ Application of ILs also was extended into areas of analytical chemistry^{10,12–14} including electrochemistry, separations, mass spectrometry, and spectroscopy. In this Account, the application of RTILs in the area of chemical separations is examined. This includes liquid–liquid extraction, liquid microextraction, solid microextraction, gas chromatography (GC), and supported liquid membranes.

2. Gas Chromatography

Early on, a series of papers reported using various quaternary ammonium and phosphonium salts as the gas chromatography (GC) stationary phase for packed and open-tubular columns.^{15–18} However, the relatively narrow liquid ranges and thermal instability of these salts limited their practical application as GC stationary phases. Thus, they were mainly of academic interest.

The unique properties of modern imidazolium-based RTILs such as high viscosity, broad liquid range, high thermostability, low volatility, good wetting ability for fused silica capillary, and the possibility of multiple interactions with a variety of solutes make these types of ILs suitable candidates for GC stationary phases coated on fused silica capillary columns. [BMIM][PF₆] and [BMIM][Cl] were evaluated as GC stationary phases on fused silica capillary columns.¹⁹ The Rohrschneider–McReynolds constants for these two IL stationary phases were determined and compared with a traditional polysiloxane stationary phase. The ionic liquid stationary phase showed a dual-nature property. That is, ILs can retain and separate nonpolar compounds as well as polar compounds.¹⁹ Using a solvation parameter model developed by Abraham (i.e., a more elaborate version of the earlier Rohrschneider–McReynolds approach), 17 RTILs were characterized with inverse GC.²⁰ The results showed that the most important interactions between RTILs and solutes were dipolarity, hydrogen bond basicity, and dispersion forces. By use of this solvation parameter approach, each ionic liquid could be characterized according to its own unique hydrogen bond acidity, hydrogen bond basicity, dipolar, $n-\pi + \pi-\pi$, and dispersion interactions. This was not only useful in characterizing and classifying ILs, but it also provided an explanation as to their effect on both organic reactions and chromatographic retention. The interaction constants further supported the previously proposed dual-nature property of IL stationary phases.²⁰ However, column bleed was observed for these IL stationary phases below 200 °C due to the decomposition or partial volatilization of the ILs. Unsymmetrical peak shapes were also observed for some classes of solutes that were proton donors (alcohols and acids). To solve these problems, new GC stationary phases based on two ILs with bulky monocations, 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([BeMIM][OTf]) and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate ([MPMIM][OTf]), were prepared.

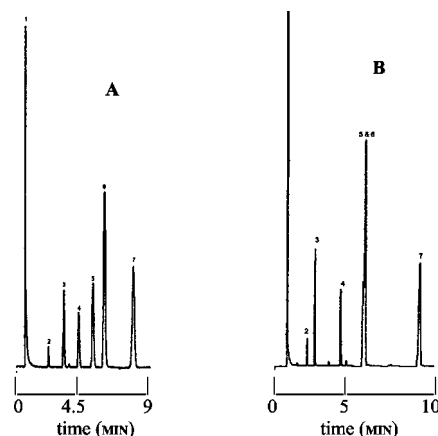


FIGURE 2. Separation of isomeric sulfoxides on (A) 10-m BeMIM–TfO column and (B) 10-m DB-17 column: 1, CH₂Cl₂; 2, *p*-trifluoromethylmethylphenyl sulfoxide; 3, *p*-fluoromethylphenyl sulfoxide; 4, *o*-chloromethylphenyl sulfoxide; 5, *m*-chloromethylphenyl sulfoxide; 6, *p*-chloromethylphenyl sulfoxide; 7, *m*-bromomethylphenyl sulfoxide. Conditions were (A) 170 and (B) 145 °C. Reproduced with permission from ref 21. Copyright 2003 American Chemical Society.

Symmetric peak shapes and high thermostabilities were observed on these two GC stationary phases. No column bleed was observed for the [MPMIM][OTf] stationary phase up to 260 °C. The separation of isomeric sulfoxides (Figure 2) and polychlorinated biphenyls on [MPMIM][OTf] column was better than that found on a commercial polysiloxane column.²¹ Subsequently, IL-GC stationary phases were compared with polar and nonpolar commercial stationary phases for the separation of volatile components of herbal plants and essential oils.²² Stationary phase mixtures of ILs and polysiloxanes gave exceptionally high efficiencies and selectivities.²²

Recently, we introduced unique types of ionic liquids that provided tremendous thermal stability and ultralow volatility. These were “multifunctional” ILs, including germinal dicationic liquids, unsymmetrical dicationic liquids, and tricationic liquids (see Figure 3).^{4,23,24} Many of these had stable liquid range from less than or equal to –8 to greater than 410 °C. It was found that some unsymmetrical dicationic liquids had melting points over 150 °C, lower than their symmetrical analogues.²³ From the standpoint of GC stationary phase stability, it was found that using functionalized ILs with vinyl groups provided the ultimate in high thermal stability and low column bleed.²⁵ This was because they could be cross-linked. A partially cross-linked IL stationary phase was used in 2-D GC for rapid separation (5 min) of a 20-component mixture and a 13-component mixture found in the headspace above U.S. currency.²⁶

A complete theoretical description of the association of alkanes with ionic liquids in dilute solution was formulated and tested using entropy and enthalpy values measured by GC.²⁷ The enthalpy can be described according to Columb’s law and following the logic of a classical Madelung-constant calculation.²⁷ The entropy can be calculated from $W(n) = n^2[2^{n-1}]W(n-1)$ where W is the number of possible rearrangements for n ion pair(s) that are ordered around or solvating a dissolved hydro-

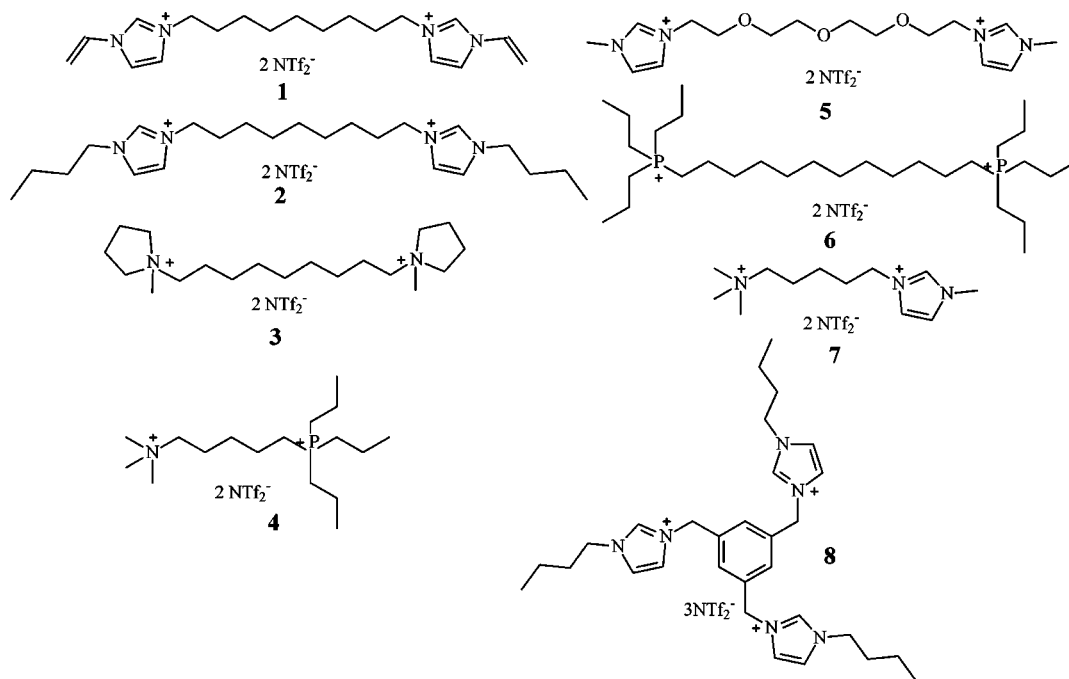


FIGURE 3. Examples of symmetric and unsymmetric dicationic ionic liquids and a tricationic ionic liquid developed in our laboratory.

carbon molecule. While more complex theoretical approaches/models can be used, as yet nothing has been shown to produce more accurate or consistent results.²⁷

ILs can be used as chiral GC stationary phases as well. Traditional chiral selectors such as derivatives of cyclodextrin were dissolved in [BMIM][Cl], and the mixture was coated on a fused silica capillary. The enantiomeric separation efficiencies of the IL columns were approximately ten times higher than comparable commercial columns with the same chiral selectors. However, the new chiral stationary phases separated fewer enantiomers. The reason for this was that the IL cation tended to occupy the cavity of the cyclodextrin and prevented the inclusion complexation of some analytes.²⁸ This was later confirmed by Tran and co-workers who measured the binding of [BMIM] to β -cyclodextrin.²⁹ Chiral ILs based on *N,N*-dimethylephedrinium bis(trifluoromethanesulfonyl)imide were coated and investigated for enantiomeric separations.³⁰ Three groups of chiral compounds including sulfoxides, alcohols, and epoxides were separated. The change of elution order was achieved by using the diastereomeric chiral ILs as stationary phases.³⁰ Development of IL chiral stationary phases with broader enantiomeric selectivity and greater thermal stability is the main challenge in this area.

ILs can also be used as solvents for headspace GC. Using imidazolium-based ILs as solvents, ethanol, ethyl acetate, cyclohexane, and toluene were detected by headspace GC.³¹ Three analytes with low vapor pressure and boiling points over 200 °C (2-ethyl-hexanoic acid, formamide, and tri-*n*-butylamine) were dissolved in ILs at the ppm level and determined by headspace GC.³²

3. Liquid-Liquid Extraction

3.1. Extraction of Metal Ions. Dicyclohexyl-18-crown-6 crown ether was dissolved in imidazolium-based ILs to extract Sr^{2+} from aqueous solution.³³ Compared with traditional organic solvents such as chloroform (distribution coefficient, $D = 0.77$) and toluene ($D = 0.76$), exceptionally large D values ($D = 10^4$ in one case) were obtained. In addition, the distribution coefficient of Sr^{2+} between the ionic liquid and water was always less than 1 without the crown ether extractant.³³ Further research showed that the distribution of alkali and alkaline earth ions depends on the hydrophobicity of the crown ether, hydrophobicity of cations and anions of ILs, and the constituents of the aqueous solution such as concentrations and characteristics of the dissolved electrolytes.^{34–36}

Calix[4]arene crown ethers were used as extractants in ILs for removal of Cs^+ from water.³⁷ Monoaza-substituted crown ethers dissolved in ILs were used to extract Na^+ , K^+ , Cs^+ , and Sr^{2+} . The ILs and crown ethers can be recycled through stripping the metal ions from the IL phase with acidic aqueous solution.³⁸ The mechanism for the extraction of Sr^{2+} from aqueous solution to the RTIL phase was investigated. When the cation of the Sr^{2+} crown ether complex moved into the IL phase, the counteranion of the IL entered the aqueous phase to maintain charge balance.³⁹ There are a number of additional reports where a combination of a chelating agent and an ionic liquid are used to extract metal ions from aqueous solution.^{40–44}

A special class of ionic liquids (named task-specific ionic liquids (TSILs)) have functional groups that permit the extraction of metal ions from aqueous solution. These ionic liquids can act as both solvents and extractants. Ionic liquids with thiourea, thioether, and urea functional groups were used to extract Hg^{2+} and Cd^{2+} from aqueous

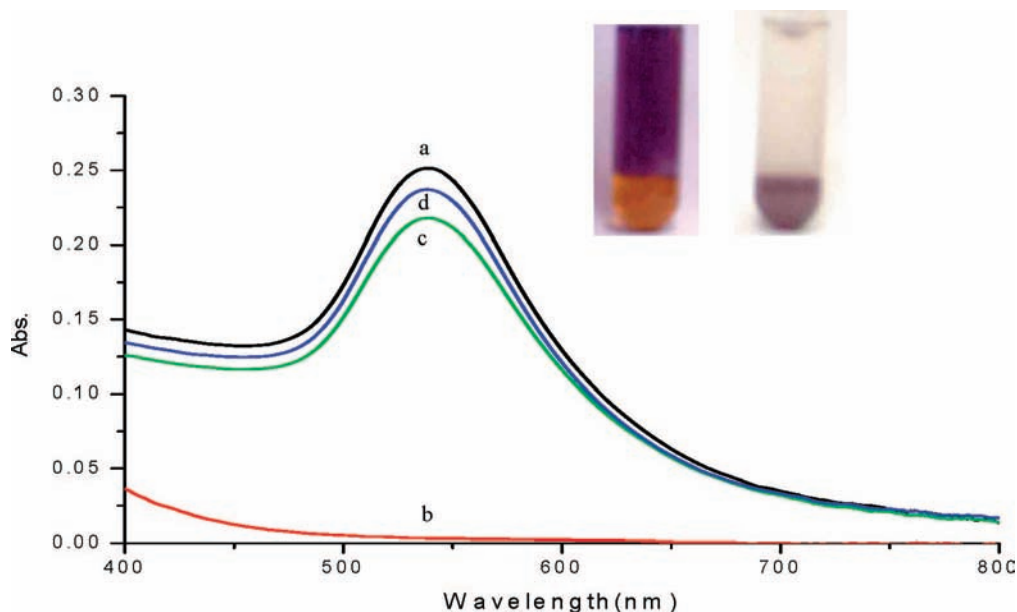


FIGURE 4. UV absorption spectra of the aqueous layer indicates the degree to which gold nanoparticles are extracted from water (curve a) to (b) benzene, (c) hexane, (d) chloroform, (e) 10-undecen-1-ol, and (f) [BMIM][PF₆]. The inset test tubes showed the gold nanoparticles before (left) and after (right) phase transfer from aqueous phase into [BMIM][PF₆]. Modified from ref 48.

solution. Significant increases in the extraction efficiency were observed for these two metal ions.⁴⁵ Another kind of TSIL used for the extraction of Hg²⁺ is an IL with a polyether-linked bis-imidazolium cation. The introduction of the ether linker in the IL increased the distribution coefficient of Hg²⁺ dramatically.⁴⁶ ILs with 2-hydroxybenzylamine fragments were employed to extract americium ions.⁴⁷

Wei and co-workers extracted gold nanoparticles and nanorods quantitatively from water to [BMIM][PF₆].⁴⁸ The size and shape of nanoparticles and nanorods did not change in the extraction process (Figure 4).⁴⁸ Cationic CdTe quantum dots were efficiently extracted into [BMIM][NTf₂] from aqueous solution and photoluminescence of these nanomaterials was enhanced in the IL.⁴⁹

3.2. Extraction of Organic Molecules. The wide application for RTILs in the extraction of organic compounds began around 1998. Rogers and co-workers determined the distribution ratio of 12 substituted benzene derivatives between [BMIM][PF₆] and water. The partitioning of these compounds between the two phases depended on both the charge and the hydrophobicity of the solutes.⁵⁰ The pH-dependent partitioning of an indicator dye, thymol blue, between [C_nMIM][PF₆] and water was demonstrated (Figure 5). Also it was shown that the distribution ratio of thymol blue between [C_nMIM][PF₆] and water increases with increasing alkyl chain length of the IL cation.⁵¹ We measured the partition coefficients for 40 compounds (including organic acids, bases, amino acids, antioxidants, and neutral compounds) at pH = 2, 5.1, and 10 between [BMIM][PF₆] and water.⁵² Distribution coefficients for the molecular form of the solutes in the IL/water system and in a 1-octanol/water system were compared. Neutral forms of ionizable compounds showed greater partitioning to the IL phase than did their ionized forms. Triphasic

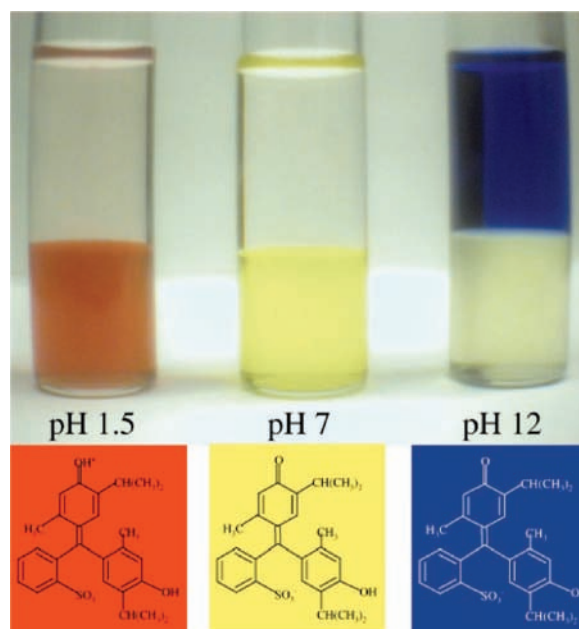


FIGURE 5. When the pH of the aqueous solution is 1.5, thymol blue is a neutral zwitterion (red color) and prefers the [BMIM][PF₆] phase (bottom layer). When the pH of the aqueous phase is 7, thymol blue is in monoanionic form. Existence of the yellow monoanion dye in aqueous phase was detectable (top layer). The blue dianion dye prefers the aqueous phase when the pH of aqueous phase is 12. Taken from ref 51 (<http://dx.doi.org/10.1039/a908888a>)—Reproduced by permission of The Royal Society of Chemistry.

systems of heptane/IL/chloroform and heptane/water/IL also were demonstrated.⁵²

In general, amino acids prefer to reside in aqueous solutions as opposed to ILs. [BMIM][PF₆] with dicyclohexyl-18-crown-6 was used to extract amino acids from acidic aqueous solution.⁵³ A heme protein cytochrome

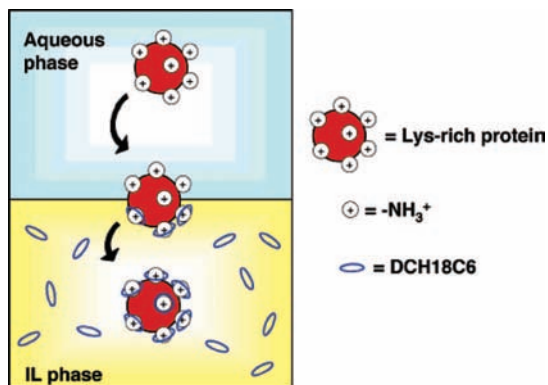


FIGURE 6. There are many NH_3^+ groups on the surface of lysine-rich proteins. The complexation of NH_3^+ groups with DCH18C6 increases the solubility lysine-rich proteins and the complexation adducts transfer from the aqueous phase to the IL phase. Reproduced with permission from ref 54. Copyright 2006 American Chemical Society.

(Cyt-c) was transferred from water to ILs bearing a hydroxyl group on the cationic moiety when dicyclohexyl-18-crown-6 (DCH18C6) was used as an additive (Figure 6). The protein showed different structure and function in the IL phase.⁵⁴ Double-stranded DNAs can be extracted into [BMIM][PF₆] directly without the interference of proteins and metal species in aqueous solutions. The extraction was due to interactions between the cation of the IL and P–O bonds of phosphate groups in the DNA.⁵⁵

The application of ILs for deep desulfurization of diesel and gasoline fuels was assessed. Sulfur-containing aromatic compounds are difficult to remove from fuels with traditional desulfurization methods.⁵⁶ However, these sulfur-containing compounds can be efficiently removed by extracting fuels with RTILs.⁵⁶ [BMIM][PF₆] and [BMIM][BF₄] with an oxidant (H_2O_2) were used to remove sulfur compounds from light oils. Sulfur-containing compounds were extracted into the IL phase and oxidized to sulfone. With this method, the desulfurization yield increased by one order of magnitude compared with a simple extraction with RTILs.⁵⁷

3.3. Recovery of Solutes Extracted in ILs and Regeneration of ILs. Distillation can be used to recover thermostable compounds with low boiling points from ionic liquids. Compounds with ionizable groups can be back-extracted into water at suitable pHs. Organic solvents that form two-phase systems with ILs can be used for the back extractions of neutral, thermally unstable compounds.^{58,60} Also the “green” solvent supercritical- CO_2 is a good choice for the recovery of solutes and the regeneration of ILs. Supercritical- CO_2 can dissolve in the ILs, while ILs cannot dissolve in supercritical- CO_2 . This unique property means that solutes can be isolated from ILs without IL contamination. It also provides a means for recycling the ILs.⁵⁸ A methanol/[BMIM][PF₆] mixture can be separated using pressurized CO_2 .⁵⁹ Aromatic and aliphatic compounds were extracted into a CO_2 phase from [BMIM][PF₆].^{58,60} A two-step extraction system (water/RTIL/ CO_2) for trivalent lanthanum and europium was reported. The metal ions were extracted from the aqueous phase into super-

critical- CO_2 via a RTIL/fluorinated β -diketonate mixture with high extraction efficiencies.⁶¹

4. Liquid-Phase Microextraction (LPME) and Solid-Phase Microextraction (SPME)

The unique properties of ILs such as high viscosity, minimal vapor pressure, and compatibility with HPLC make them suitable for LPME. Polycyclic aromatic hydrocarbons (PAHs) were enriched in a 3 μL [OMIM][PF₆] drop using both a direct-immersion and headspace method. Compared with 1-octanol, the large drop size and longer survival of IL drops resulted in higher enrichments of analytes.⁶² In other work, degradation products from surfactants were extracted into a drop of 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]). The results showed that the extraction efficiency is solute-dependent.⁶³ Chlorinated anilines in water⁶⁴ and formaldehyde in shiitake mushroom⁶⁵ were enriched by either headspace or direct-immersion using ILs.

[OMIM][PF₆] also was coated on a steel or fused-silica fiber for headspace SPME. Benzene, toluene, ethylbenzene, and xylenes in paints were enriched in the IL coated fiber and determined by GC.⁶⁶ Coating the fibers with a Nafion membrane and then absorbing the [OMIM][OTf] made a thick IL layer with higher capacity. This fiber can extract 2–3 times more PAHs compared with the fiber without the Nafion membrane.⁶⁷ Most recently, several monocationic and dicationic ILs were used to coat SPME fibers.⁶⁸ They were shown to absorb both polar and nonpolar analytes and also were compatible when coupled to GC.

5. Supported Liquid Membranes

A supported liquid membrane system includes a feed solution, a solvent or solvent/carrier immobilized in the porous structure of a polymeric or ceramic membrane, and a receiving solution. The analyte dissolved in the feeding solution goes through the membrane and is enriched in the receiving solution.^{69,70} The organic solvent supported liquid membrane is not stable because of the loss of immobilized solvent via evaporation and its dissolution in the feed or the receiving solution. The unique properties of ILs such as negligible vapor pressure and immiscibility with water and some organic solvents can overcome these problems.^{69,70} Several ILs combined with different membrane supports were investigated for the separation of a seven-component organic mixture. Different combinations produced different selectivities for specific analytes. The high selectivity of secondary amines over tertiary amines was attributed to their hydrogen-bonding interactions with the 2-position proton on the imidazolium cation.^{69,70} Hydrophobic ILs were used as membranes for the separation of aromatic and alkyl compounds.⁷¹ Tetrapropylammonium tetracyanoborate was immobilized in a ceramic nanofiltration support and then coated with a dimethylpolysiloxane layer. High selectivity of 1,3-propanediol from aqueous mixtures by vacuum pervaporation was obtained with this stable multiphase membrane.⁷²

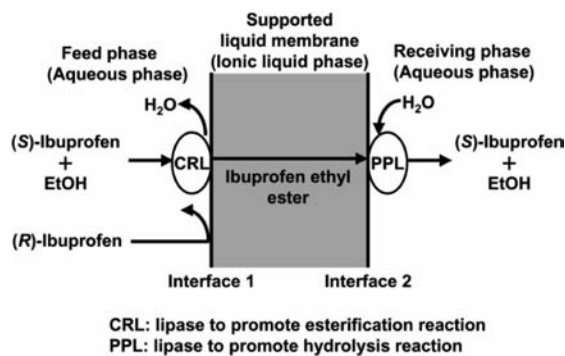


FIGURE 7. Lipase-facilitated enantioselective transport of (*S*)-ibuprofen through a supported liquid membrane containing an ionic liquid. Taken from ref 77 (<http://dx.doi.org/10.1039/b310990a>)—Reproduced by permission of The Royal Society of Chemistry.

Four different ILs were immobilized in porous hydrophilic polyethersulfone supports and examined for the flux and selectivity of CO₂/N₂ and CO₂/CH₄. The selectivities for CO₂/N₂ (61) and CO₂/CH₄ (20) were achieved with the 1-ethyl-3-methylimidazolium dicyanamide supported membrane.⁷³ Another research group used an alumina membrane filled with [BMIM][NTf₂] to achieve a selectivity of 127 for CO₂/N₂.⁷⁴ With nanofiltration membranes as support, four ILs were immobilized. The permeability of the gas molecules H₂, O₂, N₂, and CO was examined. A selectivity of 4.3 for H₂/CO₂ was achieved.⁷⁵

[OMIM][PF₆] was immobilized in a polypropylene hollow fiber and used for the hollow fiber-protected LPME of chlorophenols from natural water samples. Low HPLC detection limits and good reproducibility were obtained due to the high stability of the hollow fiber-protected IL membrane.⁷⁶

IL-supported liquid membranes also were used for the separation of a racemate. (*S*)-Ibuprofen in the feed solution was converted to (*S*)-ibuprofen ester via catalysis by a lipase, while (*R*)-ibuprofen did not react. Subsequently, the (*S*)-ibuprofen ester was transported through a [BMIM][PF₆] filled membrane, and the (*R*)-ibuprofen was rejected. The (*S*)-ibuprofen ester was hydrolyzed with the aid of another lipase in the receiving solution to recover the (*S*)-ibuprofen with an ee value up to 75% (Figure 7).⁷⁷

6. Conclusions

ILs have been widely employed in extractions, as GC stationary phases, and as supported liquid membranes. In some cases, they can be considered “green” solvents, but they have many other benefits including unusual selectivities, high extraction efficiencies, dual-nature GC properties, durability, and resistance to thermal degradations. It should be noted that the environmental benefits of ILs need be carefully considered. Recent work demonstrated the toxicity of some ILs.⁷⁸ More research is also needed on their long-term stability and recyclability. New ILs or novel applications of existing ILs can be developed that will further improve their capabilities for chemical separations. For example, the loss of ILs into aqueous media in metal ion extractions needs be suppressed. New

ILs and coating methods are being developed for high efficiency and high thermostability GC columns. Chiral GC stationary phases with high thermostability and broad enantiomeric selectivity are needed. One area that will continue to grow in importance is the use of ILs as absorbents in solid-phase extractions (SPE) and solid-phase microextractions (SPME). It is likely that ILs will fill the role of a polar absorbent for these techniques.

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