Ionic Liquids: Innovative Fluids for Chemical Processing

Joan F. Brennecke and Edward J. Maginn
Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556

Introduction

When the chemical engineering profession developed near the beginning of the last century, essentially all of the solvents available for controlling reactions, performing separations, and processing materials were already known and, to a large extent, characterized. When faced with a unit operation that called for a solvent, we turned to common liquids such as toluene, benzene, dichloromethane, acetonitrile, methanol, ethanol, and water. Despite their wide range of polarity and hydrogen-bonding ability, these common solvents are remarkably similar in one respect: they all have a relatively narrow liquidus region, ranging from 75 to perhaps 200°C. (The liquidus region is defined as the range of temperatures between the normal freezing point and boiling point. Thus, water has a 100°C liquidus range.) Because we frequently like to work with liquids, most processes have evolved under the constraints imposed by this relatively small range of temperatures.

We have used our ingenuity and the tools of chemical engineering to work within these constraints, making products that have immeasurably improved the quality of life on our planet. The benefits, however, have come with a cost. The narrow liquidus range of common solvents means that they are all relatively volatile at process conditions. Despite our best efforts and technology, including pioneering work led by AIChE's Center for Waste Reduction Technologies (http://www.aiche.org/cwrt/index.htm), an estimated *20 million ton* of volatile organic compounds (VOCs) is discharged into the atmosphere each year as a result of industrial processing operations (Allen and Shonnard, 2002).

Solvents comprise 2/3 of all industrial emissions and 1/3 of all VOC emissions nationwide. These emissions have been linked to a host of negative effects, including global climate change, poor urban air quality, and human illness. The new constraints facing chemical engineers are to continue to provide society with the products necessary for sustaining a high standard of living, while, at the same time, significantly reduce the environmental impact of the processes we use to do this. Achieving these apparently contradictory objectives is one of the great challenges facing our profession in the coming decades.

A new class of compounds has emerged in the last ten years that may become a key ally in helping us meet the twin challenges of efficient and environmentally benign chemical processing. They have the potential to revolutionize the way we think of and use solvents. They act much like good organic solvents, dissolving both polar and nonpolar species. In many cases, they have been found to perform much better than commonly used solvents. Perhaps, the most intriguing feature of these compounds is that, while they are liquid in their pure state at room temperature, they have essentially no vapor pressure. *They do not evaporate,* and so they cannot lead to fugitive emissions. Many of these compounds are liquids over incredibly large temperature ranges, from below ambient to well over 300 to 400°C, which suggests they could be used under unique processing conditions.

What are these compounds? They have become known as *room temperature ionic liquids* or simply "ionic liquids" (ILs). They are organic salts, whose cations, substituents, and anions can be varied virtually at will to change their chemical and physical properties. So far, chemical engineers have played only a small role in the early research and development activities surrounding ionic liquids. We would like to use this opportunity to bring to the forefront the many exciting challenges and opportunities available to chemical engineers in this field.

Characteristics of Ionic Liquids

Molten salts have long attracted interest and curiosity. Applications were limited, however, due to the high temperatures necessary (e.g., the melting point of NaCl is 801°C). Here, we define the term ionic liquid as a molten salt with a melting point below 100°C. Ionic liquids are organic salts, invariably possessing a high degree of asymmetry that frustrates packing and thus inhibits crystallization. The possible choices of cation and anion that will result in the formation of ILs are numerous. Examples of just five different well-known classes of ionic liquids are shown in Figure 1. Of these, the most popular are undoubtedly the di-alkylimidazolium salts, probably due to their ease of synthesis and attractive physical properties. Quaternary ammonium salts (which tend to be slightly higher melting) are available commercially and are used routinely for phase transfer catalysis. The substituents on the cations (the "R" groups) are typically alkyl chains, but can contain any of a variety of other functional groups as well (e.g., fluoroalkyl, alkenyl, methoxy, etc.).

A key feature of ILs is that their physical properties can be tailored by judicious selection of cation, anion, and substituents. As a simple example, the water solubility of the IL can be controlled by the nature of the R group. Increasing the length of an alkyl chain tends to decrease water solubility by increasing the hydrophobicity of the *cation.* In addition, chemical and physical properties can be changed dramatically by the choice of *anion,* such as halide [Cl^-, Br^-, I^-], nitrate [NO_3^-], acetate [$CH_3CO_2^-$], trifluoroacetate [$CF_3CO_2^-$], tetrafluoroborate [BF_4^-], triflate [$CF_3SO_3^-$], hexafluorophosphate [PF_6^-], and bis(trifluoromethylsulfonyl) imide [$(CF_3SO_2)_2N^-$]. For example, Seddon and coworkers (2000) provide some general guidelines on the effect of anion choice on the miscibility of ILs and water. They indicate that imidazolium salts with halide, acetate, nitrate and trifluoroacetate anions are totally miscible with water, that [PF_6^-] and [$(CF_3SO_2)_2N^-$] imidazolium salts are immiscible, and that [BF_4^-] and [$CF_3SO_3^-$] imidazolium salts can be totally miscible or immiscible depending on the substituents on the cation.

The melting points of the salts having halides for the anion tend to be somewhat higher than when bulkier anions are used, and melting point generally increases with increasing substituent chain length. Some of the first widely studied ionic liquids were actually mixtures of dialkylimidazolium or alkylpyridinium halides with $AlCl_3$ or $AlBr_3$ (Welton, 1999). These mixtures form low melting eutectics and exhibit interesting chemical properties, such as superacidity (Welton, 1999). They are also excellent nonvolatile catalysts for Friedel-Crafts alkylation and acylation reactions. They have been studied extensively for potential uses as electrolytes in batteries due to their high conductivity. Unfortunately, they react with water to form HCl, making them unstable in air and of limited practical utility. The first air and water stable ionic liquids with attractive, low melting points were 1-ethyl-3-methylimidazolium BF_4 and $MeCO_2$ (Wilkes and Zaworotko, 1992).

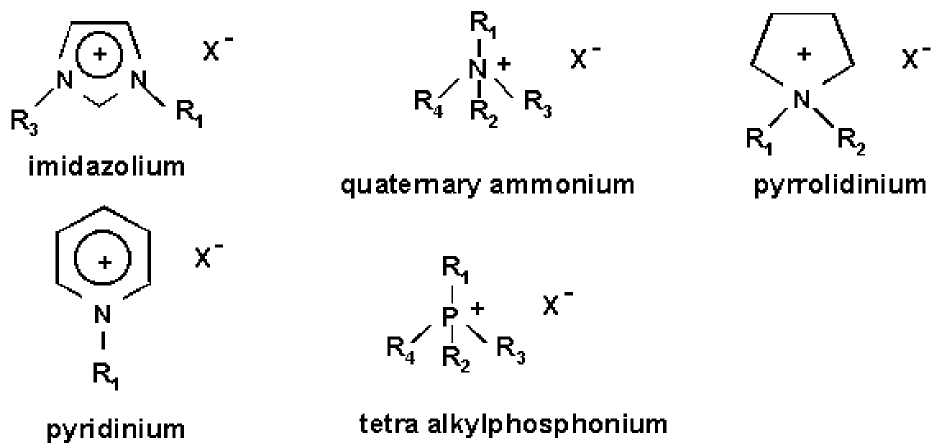

Figure 1. The anion (X^-) can be any of a variety of species: imidazolium, pyridinium, quaternary ammonium, tetra alkylphosphonium, and pyrrolidinium salts, including nitrate [NO_3^-], acetate [$CH_3CO_2^-$], trifluoroacetate [$CF_3CO_2^-$], tetrafluoroborate [BF_4^-], triflate [$CF_3SO_3^-$], hexafluorophosphate [PF_6^-], and bis(trifluoromethylsulfonyl) imide [$(CF_3SO_2)_2N^-$].

Ionic liquids of the types shown in Figure 1 tend to be somewhat more viscous than ordinary organic solvents. For instance, the viscosity of most of the dialkylimidazolium ionic liquids ranges from about 35 to 500 cP at room temperature (Seddon et al., 2001). Salts with the bis(trifluoromethylsulfonyl) imide [$(CF_3SO_2)_2N^-$] anion tend to be on the lower end of this viscosity range (Bonhôte et al., 1996), as do salts with the pyrrolidinium cation (MacFarlane et al., 1999). Our data indicate that ionic liquids (excluding those that form liquid crystals) are Newtonian fluids (Brennecke et al., 2001).

Potential Applications of Ionic Liquids

Aside from the use of quaternary ammonium salts for phase transfer catalysis and metal extraction, we know of no other examples of the commercial use of ionic liquids. We believe this will change as industrial interest grows (e.g., Freemantle, 2000) and engineers begin to address the technological challenges discussed below. Since all the potential uses of ionic liquids have not yet been developed (or thought of!), they cannot all be enumerated here. Nonetheless, below we describe some of the applications for which the unique properties of ILs may be advantageous.

Reactions. ILs have been used successfully for hydrogenations, hydroformylations, isomerizations, dimerizations, alkylations, Diels-Alder reactions, and Heck and Suzuki coupling reactions, among others. Some of these studies can be found in reviews by Welton (1999) and others (Chauvin and Olivier-Bourbigou, 1995; Seddon, 1996). In general, researchers have found that reaction rates and selectivities are as good or better in ILs as in conventional organic solvents. Recently, it even has been shown that they are excellent media for biocatalyzed reactions. Thus, it is likely that ILs will see their first major commercial application as a solvent for a reaction, particularly in the area of homogeneously catalyzed reactions. Homogeneous catalysts often impart much greater selectivity than their heterogeneous counterparts, but separation of the catalyst from the product or extract stream is frequently a problem. The partition coefficient of the most common metal-centered homogeneous catalysts greatly favors the ILs phase over an immiscible organic product or extract phase. Thus, the homogeneous catalyst remains essentially "immobilized" in the IL solvent for reuse, while separation of the products from the solvent is also made easier by the fact that the solvent itself is nonvolatile.

There is also significant potential for exploiting the ionic nature of the IL solvent to control reaction chemistry, either by participating in the reaction or stabilizing highly polar or ionic transition states. Finally, many compounds, both polar and nonpolar, dissolve readily in ILs (Blanchard and Brennecke, 2001). Thus, there is the potential to use IL solvents to carry out reactions that are traditionally multiphase (and mass-transfer limited) in a single phase. In summary, there is substantial reason to believe that ILs are excellent solvents for a wide variety of reactions. However, there have been very few measurements and essentially no modeling of the important physical properties (e.g., gas, liquid, and solid solubilities) that determine the nature or extent of the influence of the IL solvent on the reaction. Thus, the "design" of IL solvents for reactions has been empirical.

Gas Separations. Many ILs are hygroscopic, efficiently removing water vapor from gas mixtures (Anthony et al., 2001b). We have also shown that CO_2 solubility is remarkably high (Blanchard et al., 2001; Anthony et al., 2001b). For instance, at 40°C and just 50 bar pressure, the solubility of CO_2 in [bmim][PF_6] is about 0.5 mol fraction. Interestingly, the dissolution of such large amounts of CO_2 is accompanied by only a 10% increase in volume. Moreover, gas solubility can be *tailored* by choice of cation, anion, and substituents. For instance, we have found that the use of a different anion and shortening of the alkyl chain can cut the CO_2 Henry's Law constant in half. Based on the difference in solubility of various gases and vapors, we believe that there is the potential to use ILs for gas separations (Anthony et al., 2001a). This is demonstrated in Figure 2, where we show the Henry's law constants at 25°C for several gases in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), compared to values in methanol and toluene.

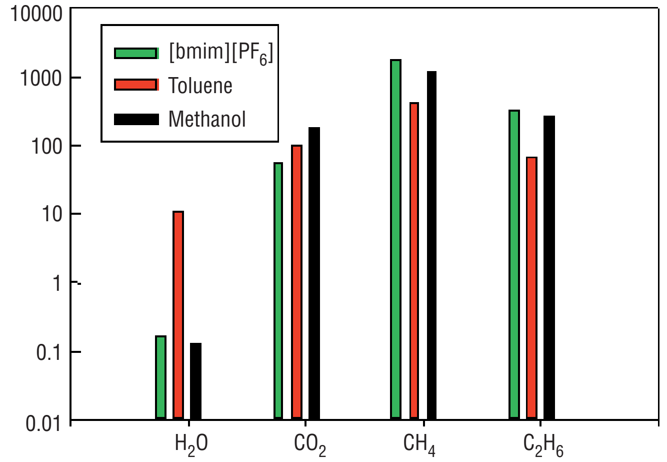

Figure 2 **Comparison of the Henry's law constants for H_2O, CO_2, CH_4 and C_2H_6 in [bmim][PF_6], toluene and methanol at 25°C.**

Since Henry's Law constants are inversely proportional to solubility, a small Henry's Law constant indicates high gas solubility. Thus, water vapor is extremely soluble in [bmim][PF_6], but methane is not, and these large differences could be exploited for gas separations. For instance, [bmim][PF_6] could be used to remove both water and CO_2 from natural gas, with anticipated selectivities, based on Henry's Law constants of 10,000 and 32, respectively. Some ILs might even be considered "pumpable adsorbents," capable of absorbing large quantities of gases at low temperature and then being regenerated at high temperature or low pressure. ILs also would be ideally suited for gas separations using a supported liquid membrane. Conventional supported liquid membranes suffer from degradation due to liquid loss from evaporation. Since ILs are truly nonvolatile, they make extremely stable supported liquid membranes (Scovazzo et al., 2001; Anthony et al., 2001c).

Liquids Separations. Since the choice of cation, anion, and substituents provides tremendous opportunity to tailor the solubility of various compounds in the IL, these new compounds should have applications in the selective separation of liquids. This concept was explored by Fadeev and Meagher (2001), who used an IL to separate alcohols from a fermentation broth. This may not be an ideal application due to relatively poor selectivity for the ILs used, and measurable solubility of the IL in the aqueous phase. Nonetheless, it suggests that with sufficient understanding of what controls IL/organic and IL/water phase behavior, ILs could be designed to perform selective liquid/liquid separations. In the same vein, Rogers and coworkers (Visser et al., 2000) have explored the use of IL/aqueous biphasic systems with added chelating agents to perform metal extractions.

Solvents for Cleaning Operations. Many ILs are remarkably good solvents for a wide variety of both polar and nonpolar compounds (Blanchard and Brennecke, 2001). For instance, the solubility of naphthalene in [bmim][PF_6] at room temperature is about 30 mol %. This is even greater than its solubility in a nonpolar solvent like *n*-hexane. However, the solubility of ethanol in [bmim][PF_6] is also quite high, compared to a low solubility of ethanol in *n*-hexane. Unlike ILs, most conventional solvents are not capable of dissolving large quantities of both nonpolar and polar compounds. As a result, ILs have potential as cleaning solvents, particularly in applications where large amounts of solvents are used to clean batch processing equipment. The disadvantage is that residual IL will remain on the surface, since the ILs are nonvolatile. Thus, a second rinse, perhaps with water, would be required, and this would create an aqueous waste stream that contains some IL. Despite this disadvantage, there may be some cleaning applications where ILs would be attractive.

Electrolytes/Fuel Cells. ILs have a number of favorable properties that make them attractive for applications in batteries and fuel cells, including a wide electrochemical window, high conductivity, a wide operating temperature range, and a low dielectric constant. In addition, their low flammability and nonvolatile nature make them safe and robust. This is one of the most well-studied application areas for ionic liquids. Several researchers are currently investigating the use of ionic liquid and polymer gel — ionic liquid electrolytes, lithium-ionic liquid batteries, and the use of ILs in photovoltaic cells.

Lubricants. We have found that ILs tend to wet metal, polymeric and inorganic surfaces. This, combined with their high thermal stability and large liquidus range makes them excellent candidates for lubricants in high-temperature and/or low-pressure applications. The temperature dependence of the viscosity appears to be similar to that of other viscous fluids, like Dow Corning 550 silicone oil. Very little research has been conducted on the potential application of ILs as lubricants.

Heat-Transfer Fluids. The desirable characteristics of a good-heat transfer fluid are a large liquidus range and good thermal stability. Some of the more common ILs (e.g., the dialkylimidazaolium salts) have exactly these characteristics. Thus, ILs have the potential to compete with even the most successful synthetic organic and silicone-based compounds in the heat-transfer fluid market. The key dimensionless parameter for heat-transfer operations is the Prandtl number, i.e., the ratio of kinematic viscosity to thermal diffusivity. Some preliminary measurements suggest that heat capacities of ILs are similar to those of heavy hydrocarbon oils and conventional organic solvents (i.e., on the order of 1–2 J g^{-1} K^{-1}). However, in general, fundamental work on heat capacities, thermal conductivities, corrosivity, toxicity, decomposition rates as a function of temperature, and the effect of impurities (like water) on all these properties is needed.

These are just a few of the many potential applications of ILs. There may also be applications in the metals and polymers industries. We hope that this article will stimulate readers to envision many more potential applications of a nonvolatile ionic liquid with tunable physical and chemical characteristics.

Challenges ... and Opportunities

Ionic liquids offer the opportunity for chemical engineers to revolutionize the way we do business. The unique properties of these liquids, and the ability to tailor properties by choice of cation, anion, and substituents, open the door to many more processing options than have been available to us using conventional organic solvents. However, there are a variety of challenges associated with turning ionic liquids from scientific curiosities into practical fluids for industrial use. These have to do with cost, lack of physical property and corrosion data, and absence of toxicity data.

Currently, ionic liquids are made primarily in laboratory-scale quantities and sell for around \$1–\$10/g. To be competitive with conventional solvents, this will have to be reduced by a factor of 100 or more (Scriven, 2001).

Design of IL solvents requires fundamental knowledge of how the nature of the cation, anion, and substituents affects chemical and physical properties. This fundamental knowledge can be developed in two ways—via targeted experimentation and through molecular thermodynamics and simulations. Because ILs are relatively new, experimental measurements of fundamental properties, like phase behavior, solubilities, heat capacities, viscosities, thermal conductivity, and electrical conductivity are extremely scarce. However, they are clearly needed. While halide-containing ILs are certainly corrosive, others appear to be much less so. However, quantitative data are not yet available. Reliable thermodynamic models of phase behavior are nonexistent.

Only recently have we and others been pursuing the use of molecular simulations to probe the properties of ILs and IL solutions (Hanke et al., 2001; Shah et al., 2001). Two distinct types of simulations are likely to be most useful in the development of ILs. On one end of the spectrum are detailed atomistic simulations employing a molecular mechanics forcefield. These simulations enable the calculation of properties essential for engineering design, including transport properties such as diffusivities and viscosities, pressure-volume-temperature properties, gas solubility, and liquid-liquid equilibria. The calculations also yield important molecular-level insight into the organization and structure of the liquid. Atomistic-level simulations are limited by the availability of accurate forcefields for ILs and, to a lesser extent, by the computational resources required to carry out the calculations. They are most useful when the goal is to obtain a maximum amount of information on a relatively small number of compounds.

At the other end of the molecular modeling spectrum are statistical cheminformatics-based modeling methods, such as quantitative structure-property relationship (QSPR) modeling. QSPR techniques have been used extensively in the pharmaceutical industry to develop libraries of lead compounds; they can function in much the same way for the development of IL libraries. QSPR modeling works by making a statistical link between the physicochemical properties of a compound and a set of molecular descriptors. These descriptors can be constitutional, topological, geometrical or electronic. Given experimental data for a small number of representative compounds (a “training set”), the method can provide pseudo-quantitative property prediction for related compounds. Importantly, properties not readily available from detailed atomistic modeling, such as toxicity and corrosivity, can be correlated with such an approach. QSPR methods are most useful when the goal is to obtain a qualitative ranking of properties for a large number of compounds.

In addition to the design of these fluids, we need to consider all other aspects of using ILs for a particular processing application. For instance, if an IL is used as a solvent for a reaction, how might one separate the reaction products from the reaction mixture without resorting to liquid/liquid extraction with a conventional VOC solvent? Volatile products could easily be evaporated, but solids or low-volatility liquids are more problematic. As one alternative, we have shown that it is possible to remove relatively low-volatility compounds from such a mixture by extraction with supercritical CO_2 (Blanchard et al., 1999).

Another important issue is how to efficiently remove ILs from aqueous streams that they may have entered in the process operation. This points to one of the major challenges in the development and commercial adoption of ILs. Specifically, the ecotoxicity and ecological impact of most ILs of the types shown in Figure 1 are not well known. Since ILs are nonvolatile, it is clear that the most likely medium for their introduction into the environment will be aqueous streams. Thus, work is desperately needed to determine which ILs have the least negative impacts on aquatic environments. An added challenge is that toxicity is not even known for many classes of ILs. For instance, the first mammalian toxicity study for an imidazolium-based salt, indicating relatively low toxicity, appeared in the literature very recently (Pernak et al., 2001). Thus, it is important that chemists and chemical engineers work with toxicologists and ecologists in the development of these interesting new solvents.

Even if all of the technical challenges are overcome, the barriers inhibiting the adoption of ionic liquids by the chemical industry are still huge. Since the current economic structure of the chemical industry is such that returns on investment are low, technologies requiring large capital expenditures are unlikely to be adopted (Harold and Ogunnaike, 2000). This barrier has seriously limited the more widespread use of many other promising technologies. Ionic liquids may be different. The major cost associated with adopting ionic liquids in many of the applications we have outlined is the cost of the ionic liquid itself, not the capital equipment associated with the technology. It is entirely likely that they can be used with existing equipment in many of the applications described above. This is in striking contrast to technologies like supercritical fluids and adsorption, which have seen more limited use due to the high capital cost associated with their adoption. Furthermore, ionic liquids are a flexible technology. The properties can be tailored by judicious choice of the cations, anions, and substituents. Thus, they represent literally thousands of different compounds with dramatically different properties. This gives engineers many more options in optimizing these materials for a given process.

All of this demonstrates how critical it is that *chemical engineers* become involved in the development, testing, and commercialization of ionic liquid solvents. In the last 3–4 years, the growth of interest in ionic liquids as potential nonvolatile replacements for conventional organic solvents has been tremendous. The number of publications on ILs has increased from about 25–30 per year in the period 1991–1998 to about 250 in the January–September period of 2001. ILs have been the subject of numerous articles: Freemantle (1998, 1999a,b, 2000, 2001), Anonymous (1999), Guterman (1999), Chang (2001), and Renner (2001). The bulk of investigations on ionic liquids have focused on their use as solvents for reactions. This emphasis has meant that chemists have made almost all of the contributions to this emerging field. Until recently, chemical engineers have been virtually absent from any investigations or development of these new solvents. One of us (JFB) was the only chemical engineer of approximately fifty attendees at a NATO Workshop on Ionic Liquids held in April, 2000. Chemical engineers made up only a handful of those participating in a five-day symposium dedicated to ionic liquid research at the April 2001 American Chemical Society national meeting (see http://bama.ua.edu/~rdrogers/sandiego/).

Achieving the full potential of these exciting new classes of solvents will require that chemical engineers bring to bear the full assortment of our unique mathematical and technical skills on the many problems involved in the design and development of ionic liquids for practical applications. We need to be involved in the development of ILs as reaction solvents, but also look for other applications for which the properties of these interesting nonvolatile liquids can be exploited. The primary challenges of turning ionic liquids into useful and environmentally benign industrial fluids are twofold.

First, we must use our creativity to envision the many applications in industries such as chemical processing, pharmaceuticals, fine chemicals, petroleum refining, microelectronics, metal refining and finishing, polymer processing, pulp and paper, and textiles where a nonvolatile liquid with a wide liquidus range could work better and, concomitantly, reduce emissions and air pollution. Chemical engineers uniquely have knowledge of practical applications where nonvolatile solvents may be advantageous, an understanding of the important physical and chemical properties that are necessary for those applications, and the skills to design and develop IL solvents tailored for those applications. Many applications of ionic liquids are unlikely to be anticipated by researchers in other disciplines.

Second, we must promptly marshal our energies and intellects to get in on the ground floor in the development of ILs. With specific applications in mind, we need to help set the tone and direction of the research and development activities going on in this field. If chemical engineers do not step up to this challenge, it is likely that many of the issues critical for turning ILs into commercially viable products will continue to be unaddressed. We have the opportunity to participate in the design of fluids that could greatly improve numerous chemical processes while at the same time reduce emissions to the environment. The challenge is to not miss the opportunity.

Literature Cited

Allen, D. T., and D. R. Shonnard, *Green Engineering*, Prentice Hall, Upper Saddle River, NJ (2002).

Anonymous, "Ionic Solvents; A Working Solution?" *The Economist,* **351**(82) (June 19, 1999).

Anthony, J. L., E. J. Maginn, and J. F. Brennecke, "Gas Solubilities in 1-*n*-Butyl-3-Methylimidazolium Hexafluorophosphate," *ACS Symp. Ser.,* R. Rogers and K. Seddon, eds., in press (2001a).

Anthony, J. L., E. J. Maginn, and J. F. Brennecke, "Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water," *J. Phys. Chem. B,* in press (2001b).

Anthony, J. L., Z. Gu, L. A. Blanchard, E. J. Maginn, and J. F. Brennecke, "Gas Solubility in Ionic Liquids," ACS Meeting (Apr., 2001c).

Blanchard, L. A., D. Hancu, E. J. Beckman, and J. F. Brennecke, "Ionic Liquid/CO_2 Biphasic Systems: New Media for Green Processing," *Nature,* **399,** 28 (1999).

Blanchard, L. A., and J. F. Brennecke, "Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.,* **40,** 287 (2001).

Blanchard, L. A., Z. Gu, and J. F. Brennecke, "High-Pressure Phase Behavior of Ionic Liquid/CO_2 Systems," *J. Phys. Chem. B,* **105,** 2437 (2001).

Bonhôte, P., A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Gratzel, "Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts," *Inorg. Chem.,* **35,** 1168 (1996).

Brennecke, J. F., L. A. Blanchard, J. L. Anthony, Z. Gu, I. Zarraga, and D. T. Leighton, "Separation of Species from Ionic Liquids," *ACS Symp. Ser.,* M. Abraham and L. Moens, eds., American Chemical Society, Washington, DC, in press (2001).

Chang, K., "With a Splash of Salt, Industry May Reap Environmental Advantages," *New York Times*, p. D2 (Apr. 24, 2001).

Chauvin, Y., and H. Olivier-Bourbigou, "Nonaqueous Ionic Liquids as Reaction Solvents," *Chemtech,* **26** (Sept. 1995).

Fadeev, A. G., and M. M. Meagher, "Opportunities for Ionic Liquids in Recovery of Biofuels," *Chem. Commun.,* 295 (2001).

Freemantle, M. "Ionic Liquids Show Promise for Clean Separation Technology," *Chem. Eng. News,* **76,** 12 (Aug. 24, 1998).

Freemantle, M. "Ionic Liquids Prove Increasingly Versatile," *Chem. Eng. News,* **77,** 23 (Jan. 4, 1999a).

Freemantle, M. "Green Process Uses Ionic Liquid and CO_2," *Chem. Eng. News,* **77,** 9 (May 10, 1999b).

Freemantle, M. "Eyes on Ionic Liquids," *Chem. Eng. News,* **78,** 37 (May 15, 2000).

Freemantle, M. "Benign, Continuous, and Homogeneous," *Chem. Eng. News,* **79,** 41 (Sept. 3, 2001).

Guterman, L., "Ionic Solvents Opening a New Realm of Chemistry," *Chemistry* (Summer 1999).

Hanke, C. G., S. L. Price, and R. M. Lynden-Bell, "Intermolecular Potentials for Simulations of Liquid Imidazolium Salts," *Mol. Phys.,* **99,** 801 (2001).

Harold, M. P., and B. A. Ogunnaike, "Process Engineering in the Evolving Chemical Industry," *AIChE J.,* **46,** 2123 (2000).

MacFarlane, D. R., P. Meakin, J. Sun, N. Amini, and M. Forsyth, "Pyrrolidinium Imides: A New Family of Molten Salts and Conductive Plastic Crystal Phases," *J. Phys. Chem. B,* **103,** 4164 (1999).

Pernak, J., A. Czepukowicz, and R. Pozniak, R., "New Ionic Liquids and Their Antielectrostatic Properties," *Ind. Eng. Chem. Res.,* **40,** 2379 (2001).

Renner, R. "An Environmental Solution," *Scientific American,* **285**(2), 19 (Aug. 2001).

Scovazzo, P., A. E. Visser, J. H. Davis, Jr., R. D. Rogers, R. D. Noble, and C. Koval, "Supported Ionic Liquid Membranes and Facilitated Ionic Liquid Membranes," ACS Meeting (April 2001).

Scriven, E. F. V., Reilly Industries, personal communications (2001).

Seddon, K. R., "Room-Temperature Ionic Liquids: Neoteric Solvents for Clean Catalysis," *Kinetics and Catalysis,* **37,** 693 (1996).

Seddon, K. R., A. Stark, and M. J. Torres, "Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids," *Pure Appl. Chem.,* **72,** 2275 (2000).

Seddon, K. R., A. Stark, and M. J. Torres, “Viscosity and Density of 1-Alkyl-3-Methylimidazolium Ionic Liquids,” *ACS Symp. Ser.,* M. Abraham and L. Moens, eds., American Chemical Society, Washington, DC, in press (2001).

Shah, J., E. J. Maginn, and J. F. Brennecke, “Thermodynamic Properties of 1-*n*-Butyl-3-Methylimidazolium Hexafluorophosphate from Monte Carlo Simulations,” *Green Chemistry,* submitted (2001).

Visser, A. E., R. P. Swatloski, W. M. Reichert, S. T. Griffin, and R. D. Rogers, “Traditional Extractants in Nontraditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids,” *Ind. Eng. Chem. Res.,* **39,** 3596 (2000).

Welton, T., “Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis,” *Chem. Rev.,* **99,** 2071 (1999).

Wilkes, J. S. and M. J. Zaworotko, “Air and Water Stable 1-Ethyl-3-Methylimidazolium Based Ionic Liquids,” *J. Chem. Soc., Chem. Commun.,* 965 (1992).