

Ionic Liquids: Innovative Fluids for Chemical Processing

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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^-], trifluo-