Opportunities for commercializing ionic liquids

Interest in ionic liquids has grown exponentially in the past decade. Although these salts with low melting points were described in the late 19th century, serious efforts to understand this class of materials and develop their commercial potential only began in the 1970s.
Different groups, depending on the focus of their particular interests, have described this large and growing class of novel materials in a number of ways:

"Organic salts with melting points under 100°C, often below room temperature"
"Liquids... composed entirely of anions and cations in contrast to molecular solvents"
"Liquids with a wide temperature range and no vapour pressure"
"Fused salts are liquids containing only ions"
"Salts that are liquid over a wide temperature range including room temperature"

The key features that underlie most of these definitions are that these materials have 1) a **large liquid range** and 2) **no measurable vapour pressure**, owing to their being composed of ions rather than discrete molecules.

PROPERTIES OF IONIC LIQUIDS

Typical characteristics or properties generally associated with ionic liquids are listed in Table 1. It is this novel collection of properties that makes ionic liquids commercially interesting.
The number of possible ionic liquids is virtually unlimited.Because of the susceptibility of both the cation and the anion to multiple permutations, millions of ionic liquids can be created from a few standard building blocks.
One way to categorize ionic liquids is by the interaction of the anion with water. Using this criterion, they can be grouped into three classes:

- The **water reactive class** includes the chloroaluminates that were among the first to be developed (by Wilkes and co-workers) and later formed the basis for extensive commercial development of Friedel-Crafts acylation and olefin dimerization.
- The **water miscible class** can be represented by the halides, simple anions like nitrates, acetates, triflates, fluoroborates, and other anions.
- The **water immiscible class** includes hexafluorophosphates, imides, FAP, and BR4.

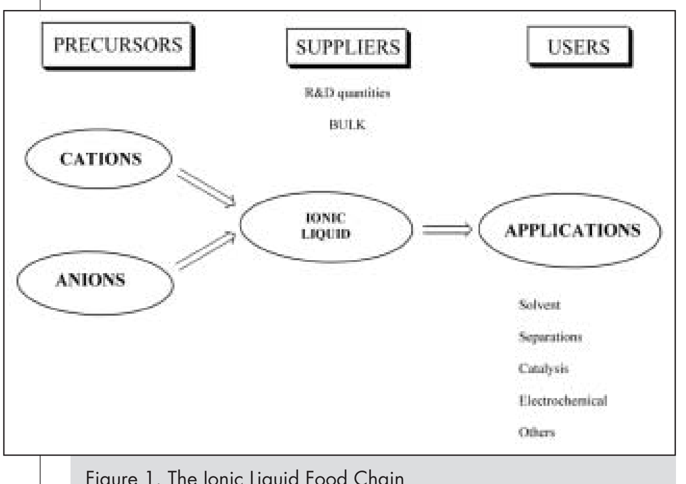

Figure 1. The Ionic Liquid Food Chain

Water miscibility has important implications for the way ionic liquids are put to commercial use. Within the most widely studied groups of cations (the imidazolium and pyridinium cations), water miscibility can be altered by either changing the anion or changing the substitution on the cation. This has lead Professor Jim Davis at the University of South Alabama to refer to these materials as "task specific" ionic liquids.Ionic liquids also have been called "designer solvents," but this definition is far too narrow.

DESIGNING AN IONIC LIQUID

Designing an ionic liquid for a specific task involves looking at the individual components–the cation and the anion. Various properties of the final material are influenced by either the cation, anion, or both (Figure 2).

- Cations influence **toxicity** by virtue of the chain length on (for example) alkyl ammoniums. Phosphoniums are far less toxic than their nitrogen counterparts. Other things being equal, the anion has very little influence on toxicity.
- **Biodegradability** often depends on the chain lengths on the (typically organic) cation; simple anions (acetate, nitrate, etc.) are generally not a concern
- **Water miscibility** also depends on cation alkyl chain length
- **Water miscibility** can also be controlled by choice of anion – e.g., PF_6 vs. BF_4 or nitrate
- **Stability in the presence of water** is usually a function of the anion – e.g., $AlCl_4$ and the issue of the stability of PF_6 and BF_4

Many anions with desirable properties, like triflimide, are currently very expensive. Developers of designer ionic liquids or task specific ionic liquids would prefer to rely on readily available starting materials. Naturally occurring chiral centres offer an attractive means of building this property into a "task specific" ionic liquid.

FACTORS CREATING OPPORTUNITIES FOR IONIC LIQUIDS

Several trends within the chemical industry are creating opportunities for ionic liquids. These include:

- The increasing regulation of volatile organic compounds (VOCs)
- Developments in "clean" or "atom efficient" synthesis
- Higher energy costs driving greater efficiency in chemical processing

Certainly the first factor (VOC) is one where ionic liquids bring value. In many applications, higher energy costs may be offset, provided that the ionic liquids themselves can be manufactured and used economically.

STRUCTURE OF THE IONIC LIQUID FOOD CHAIN

There are at least three ways for companies to participate in the commercialization of ionic liquids. These opportunities might be described as the three parts of the "food chain" illustrated in Figure 1.

- Making the component parts of the ionic liquids–the cations or anions
- Assembling and marketing the ionic liquids itself
- Using the ionic liquid in some industrial process or product

A given company may be involved in more than one step in this food chain and its participation can evolve over time.

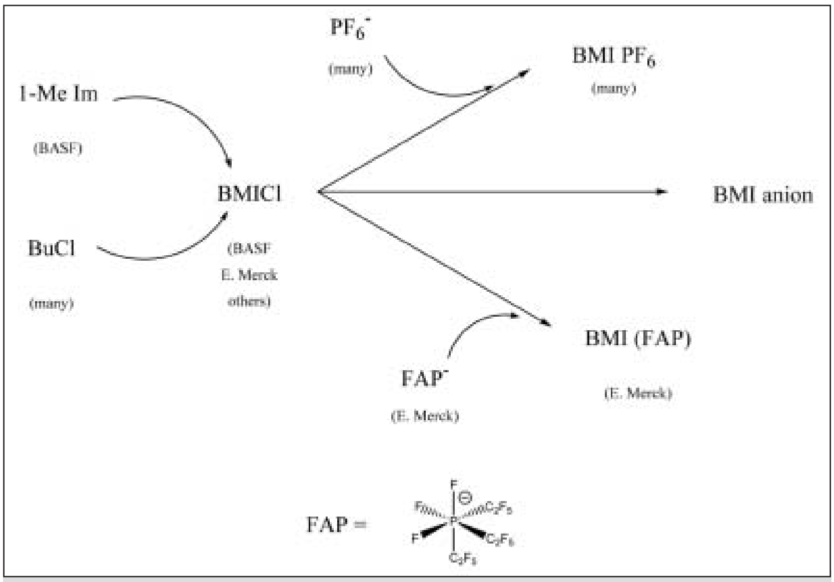

Figure 2. The Imidazole Food Chain

MAKING THE COMPONENTS

A large number of companies supply or are capable of supplying the major cations used in ionic liquids, including imidazolium, pyridinium, ammonium and phosphoniums. Many are actively marketing their capabilities either as component suppliers or as assemblers and marketers of finished ionic liquids.
On the anion side, there are fewer companies with an active marketing effort directed to ionic liquids. A few suppliers are basic in fluoride-based anions. Merck is noteworthy in this regard, having designed the FAP anion, a PF_6 substitute with good stability against hydrolytic degradation to HF. Several of the common anions (e.g. nitrate, acetate, etc.) are widely available.

Ionic in composition with m.p. < 100C
Negligible vapor pressure and miniscule flammability
Large liquid ranges
Good thermal stability
Variable polarity and ionic strength
Good dissolving power, yet non-coordinating
High heat capacity
Susceptible to multiple permutations

Table 1. Typical properties of ionic liquids

Cations influence:	Anions influence:
Water miscibility	Water stability
Toxicology	Water miscibility
Biodegradability	Viscosity
Viscosity	Cost
Cost	

Table 2. Controlling the Properties of Ionic Liquids

ASSEMBLING THE COMPONENTS

There is no shortage of suppliers of ionic liquids in research quantities. Most of the major R&D catalogue houses carry a representative line. ACROS, for example, has a marketing arrangement with QUILL to make available for research ionic liquids from that laboratory.
Several producers of cations or anions offer to sell or, in some cases, give free samples of ionic liquids containing their particular cation or anion, so as to promote development efforts to commercialize products and processes based on the building block they supply.
Several companies in Europe have made a commitment to the scale-up of ionic liquids to the commercial scale. Prominent among them are Solvent-Innovations, a start up from Prof. Dr. Peter Wasserscheid's research group in Aachen, E.Merck (or EMD as it is called in the US), BASF and Degussa.
As an example, BASF participates in all three steps of the ionic liquid food chain (Figure 2).It may be regarded initially, as a component supplier (as a producer of 1-methylimidazole, a precursor to the imidazolium ionic liquids).It subsequently commercialized a process using 1-methylimidazole (the BASIL process) and is offering licenses of this technology. Later, it introduced a commercial line of ionic liquids based on their raw material position and applications experience.
E. Merck has committed to an extensive business and marketing effort, and has developed a broad range of ionic liquids, including several novel, patented substitutes for the PF_6 anion. Merck has also built an extensive database with hundreds of different compounds that it is prepared to supply in bulk.
Figure 2 illustrates the imidazole food chain, showing where some of the pieces of the final ionic liquids come from and how BASF and Merck fit in.
Note that BMI chloride itself is positioned as an ionic liquid since there is developing commercial applications work using BMI chloride as a solvent for cellulose extraction.
Figure 2 also shows the structure of the novel FAP anion developed, patented and commercialized by Merck as a more robust alternative to PF_6. Of course, there are many other BMI or indeed alkyl(methyl)imidazole derivatives.
Another important component supplier is CYTEC, a well-known producer of **phosphonium** halides. They also offer phosphonium-based ionic liquids for potential commercial development. CYTEC is basic in phosphines and phosphonium cations and has developed extensive data on the use of these materials as extractants and as phase transfer catalysts.
Figure 3 shows the classical route to the phosphonium chloride, followed by metathesis to replace the chloride with other anions. However, interest in "halogen-free" ionic liquids has led to considerable effort to develop "chloride-free" synthetic routes such as the one shown in Figure 4. The direct reaction of trialkyl phosphines with, for example, a sulfonic acid ester, gives the final ionic liquid in a one-pot, atom-efficient-reaction.

APPLICATIONS OF IONIC LIQUIDS

In recent years, research into possible applications of ionic liquids has exploded. Tens of thousands of reactions, traditionally carried out in classical solvents, have been repeated in various ionic liquids, often with unsurprisingly similar results. More than a decade of extensive research has yet to uncover the "killer application" that will put ionic liquids on the commercial map and generate hundreds of millions of dollars in revenue. And that may not happen. The sheer diversity of possibilities both in the structure of the ionic liquid, and in the areas of potential application, suggest that this field will grow a multitude of fragmented uses. In each, a specific

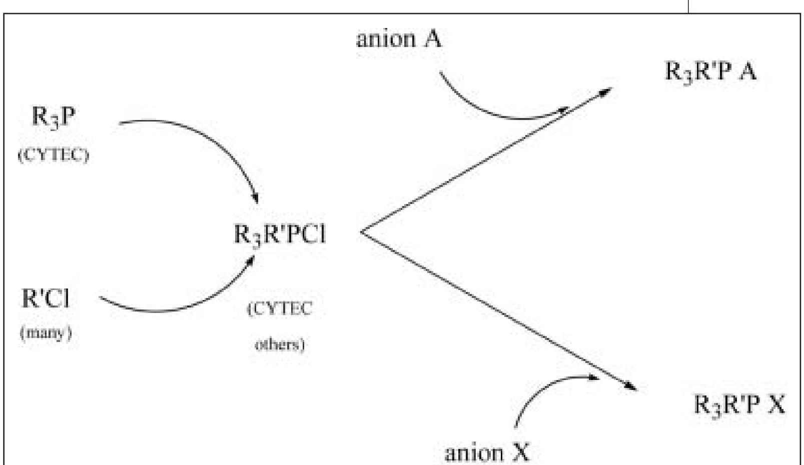

Figure 3. Routes to phosphonium based ionic liquids

ionic liquid will be adopted for its unique properties. Table 3 summarizes the numerous areas of application currently being explored.

Solvents and catalysts:
- Innocent (non-interacting) solvents
- Ligand precursors
- Co-catalysts

Extractions and separations:
- Desulfurization of fuel
- Treatment of nuclear waste
- Cellulose reprocessing (biomass conversion).
- Gas separation (Brennecke patents).

Biotechnology
- Enzyme catalysis
- Protein syntheses

Nanotechnology

Storage and delivery of hazardous gases

Electrochemical applications
- Fuel cells
- REM (reversible electrochemical mirrors)
- Electrolytes in batteries
- Electrolytes in sensors
- Metal plating

Engineering Fluids:
- Lubricants
- Thermodynamic fluids

Performance Additives:
- Lubricants
- Stabilizers
- Plasticizers
- Heat transfer fluids
- Coatings
- Cleaning agents.
- Dispersants
- Base oils for rolling aluminum sheet.
- Heat transfer fluids

Table 3. Application areas for ionic liquids

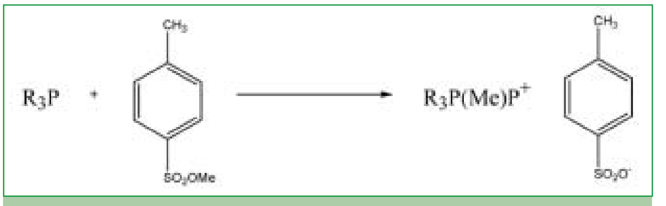

Figure 4. One-pot chloride free synthesis of ionic liquids

A WORD ABOUT COSTS

Catalogue prices for 100 gm quantities should not be used as a guide to commercial utility. Nor should cost by itself be an impediment to commercial development. If an ionic liquid is being considered as a component to an industrial process (as, for example, a solvent), it is important to investigate the synthetic route to that ionic liquid and evaluate the cost of the building blocks. For example, imagine a process using the ionic liquid $BMIPF_6$. The readily available starting materials for constructing this ionic liquid are 1-methylimidazole, butyl chloride and the PF_6 anion (from either HPF_6 or KPF_6). Nothing on this list costs over $5/kg in ton quantities.
To be cost effective, ionic liquids will need to be recycled. Solving the "cleanup" problem is vital. If the chosen ionic liquid is inherently safe from a toxicological point of view, workplace safety and personnel protection costs can be reduced. These benefits, however, may be offset by the one-time cost of new compound registration, which weighs heavily on those seeking to commercialize a new chemical substance.
Finally, cost will depend on value. If, by using an ionic liquid in his process, a customer can save 2 cents/kg on a million kilograms, maybe he can afford to pay $300/kg for the ionic liquid.

THE FUTURE

The future of ionic liquids will branch into two directions.One will evolve for large-scale bulk applications where cost is important, where robustness and tolerance of impurities and recycling are critical and where the application qualifies as "environmentally sound."
The second direction leads to boutique (task specific, optimized for performance) applications where these ionic liquids are used for their intrinsic properties and are designed to specific and unique applications. Here cost will be less important, because the ionic liquid may be the only way to do a particular task.
In the near future several examples of both bulk and boutique ionic liquids will become commercial. There will be many uses in multiple markets, with no single dominant market.
Worldwide the ionic liquids business could exceed $50 million annual in a very short time.

PHILIP E. RAKITA

**Armour Associates, Ltd.
185 Haywood Knolls Drive
Hendersonville, NC 28791 (USA)**