Overview: Technical Summaries on Ionic Liquids in Chemical Processing

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“Barriers to Ionic Liquid Commercialization”
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Acknowledgments

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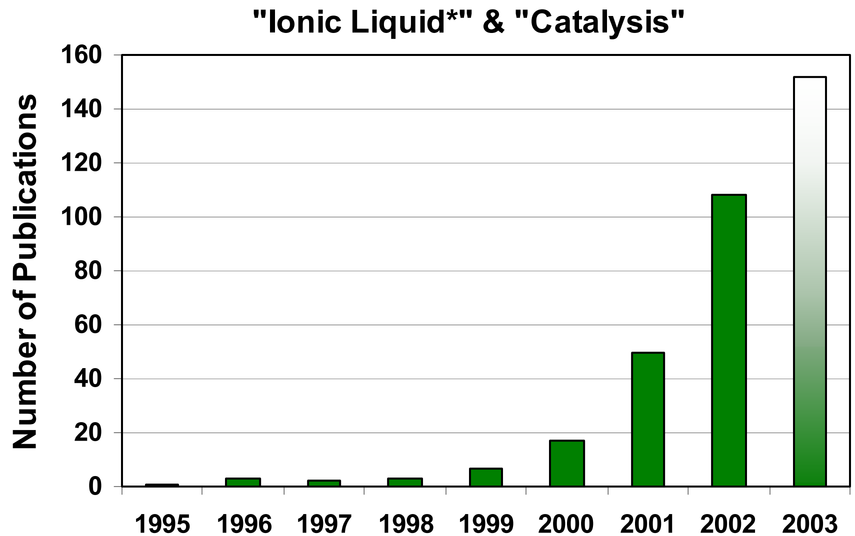
Purpose

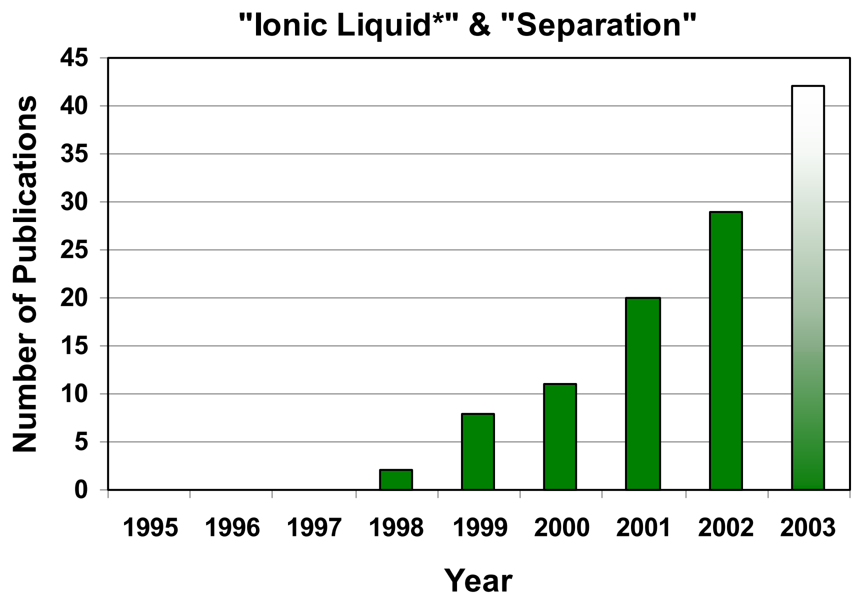
- Provide common starting point for discussions in workshop aimed at creating a roadmap that will address key challenges for the commercial applications of ionic liquids

- Identify key accomplishments and challenges in four areas
  - Catalysis
  - Separations
  - Fuels
  - Polymerization

Tremendous growth in R&D on application of ionic liquids to chemical processing

- **Active research**
  - Industry
  - Academia
  - Government labs
- **Rapidly increasing publication rate**
- **Increasing patent activity**
  - New ionic liquids
  - Application of ionic liquids for chemical processing





Recent progress in commercialization of ionic liquids

Davis & Fox, *Chem. Commun.*, 1209-1212 (2003).

FOCUS ARTICLE

ChemComm www.rsc.org/chemcomm

From curiosities to commodities: ionic liquids begin the transition

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A growing variety of ionic liquids are becoming commercially available, a development that will feed the surge of research using these unorthodox liquids.

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INDUSTRIAL CHEMISTRY

BASF'S SMART IONIC LIQUID

Process scavenges acid on a large scale without producing solids

MICHAEL FREEMANTLE

BASF is employing an ionic liquid in the manufacture of alkoxyphenylphosphines--the first commercial use of the versatile materials in an organic process.

The company, based in Ludwigshafen, Germany, tells C&EN that it uses *N*-methylimidazole to scavenge acid that is formed in the process. The reaction results in the formation of the ionic liquid *N*-methylimidazolium chloride (Hmim-Cl), which has a melting

Supply

- Expanding number of new ionic liquids
- Increasing availability from multiple vendors

Demand

- Industrial application
- New patents

Catalysis

- **Significant academic and industrial work**
  - **Reviews:** Dupont et al. 2002; Olivier-Bourbigou & Magna 2002; Zhao et al. 2002; Sheldon 2001; Gordon 2001; Wasserscheid and Keim 2000; Holbrey and Seddon 1999; and Welton 1999

- **Highlights:**
  - **Solvents for transition-metal catalysis**
    - **Enhanced activity, selectivity**
  - **IL with an active role in the chemical reaction or catalysis**
    - **Lewis acid**
    - **Reactions with aromatic rings**
  - **In-situ catalysis directly in ionic liquid**
    - **Biphasic, triphasic catalysis**
  - **Support for heterogeneous catalysis**

  - **Current or Near-Term Applications of IL in industry**
    - Biphasic butene dimerization that uses an IL as a support for a catalyst (Dimersol, Difasol) – commercialized by IFP (Olivier-Bourbigou and Magna 2002).
    - Use of chloroaluminate(III) for polymerization of olefins – replace industrial Cosden process (Holbrey and Seddon 1999)
    - Production of fine chemicals and pharmaceuticals (Sheldon 2001)

Catalysis Challenges

- Moisture sensitivity
- Control
  - mixtures of products
  - post-catalytic separations (remove products from IL without removing catalyst).
- Cost
  - e.g., analysis for ethylbenzene production indicates an increase by factor of 5-6 with IL (Atkins et al. 2003)
- Synthesis of new task-specific ionic liquids.
- Determination of the synergistic role played by ionic liquids in enhancing catalytic processes.
- Biocompatible ionic liquids for enzyme-catalyzed reactions.

Separations

- Less overall activity than catalysis in research and application; published work since ca. 1998
- Highlights:
  - Liquid extraction from aqueous solutions
    - Organics (partitioning)
    - Metals (extractants in RTILs; “task-specific” RTILs)
  - Hydrocarbon processing
    - Sulfur removal
    - Selective separations by solubility, extractive distillation, etc.
  - Gas separations
    - Solubilities
    - Task-specific liquids
  - Solvent regeneration
    - Supercritical fluids
    - Pervaporation, distillation
  - Supported liquid membranes
  - Electrorefining
  - Analytical separations

Separations Challenges

- **Loss**
  - **- liquid extraction**
- **Instability**
  - **e.g., PF_6^- generates HF** Swatloski *et al.* (2003)
- **Regenerability**
  - **- e.g., factors that make IL's good solvents for metal-ion extraction make them difficult to extract**

Fuels

- **Significant academic and industrial interest, with potential for high-volume, energy-saving applications**
- **Highlights**
  - **Liquefaction, gasification and chemical modification of solid fuels (coal, oil shale, kerogen)**
  - **Sweetening of sour gas**
  - **Optimization for high-octane fuel additives**
  - **Environmental removal of contaminants from waste streams**
  - **Desulfurization of fossil fuels**
  - **Nuclear fuel cycle**

Fuels Challenges

- Cost
  - High-throughput processes
- Toxicity
- Demonstration on real, multicomponent process streams
  - Economics
- Stability
- Transport properties

Polymerization

- **Research published since early 1990's; significant opportunity to replace solution polymerizations using VOCs**

- **Highlights:**
  - **Homopolymerization**
    - **Faster rates**
    - **Yield polymers with higher MW**
  - **Living Radical Homopolymerization**
    - **Retain catalyst in IL phase**
  - **Statistical Copolymerization**
    - **may create copolymers having monomer sequences not readily achievable using conventional solvents**
  - **Block Copolymerization**
    - **IL routes may simplify, reduce cost of producing block copolymers with defined structures**
  - **Polymer-ionic liquid composites**
    - **New materials possible**

Polymerization Challenges

- **Poor understanding of optimizing IL for a particular polymerization**
  - **polymer isolation and purification**
    - **solubility of polymers in ILs**
  - **IL recycling**
  - **toxicity**
- **Need cheaper, less toxic, and readily available ILs.**
- **Need better understanding of core variables controlling polymerization reactions in IL media**

Cross-cutting Issues

- Uncertainty on toxicity and potential environmental impact
  - Small amount of data, but increasing activity
- Cost
- More ionic liquids are possible than can be tested
- Research primarily aimed at discovery; little process engineering data published
  - Solvent regeneration
  - Solvent lifetime with repeated cycling
  - Losses
  - Design of unit operations for IL properties
  - Process economics

Cross-cutting Needs

- Knowledge of thermophysical and chemical properties needed to implement in process simulators to reduce uncertainty in industrial application
  - Measure properties
  - Predict thermophysical and chemical properties
    - Correlations
    - Validate computational chemistry models
  - Developing-structure property relationships
  - Public web-based database

- Production and Analysis
  - reproducible production in high purity
  - facile methods of assessing purity

Summary

- **The technical community has made major strides over the past several years in R&D on the application of ionic liquids in chemical processing**
- **The first industrial applications are underway, and more can be expected.**
- **There may be opportunity to accelerate commercialization by addressing cross-cutting needs**