

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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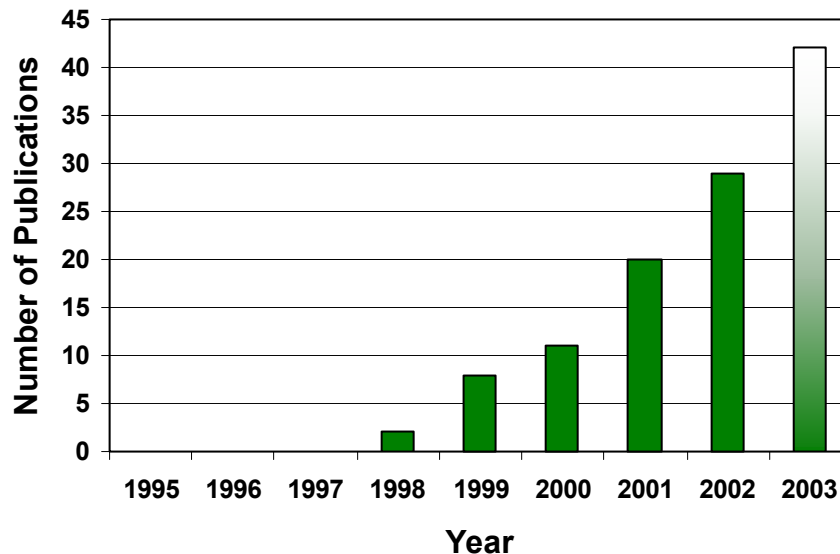
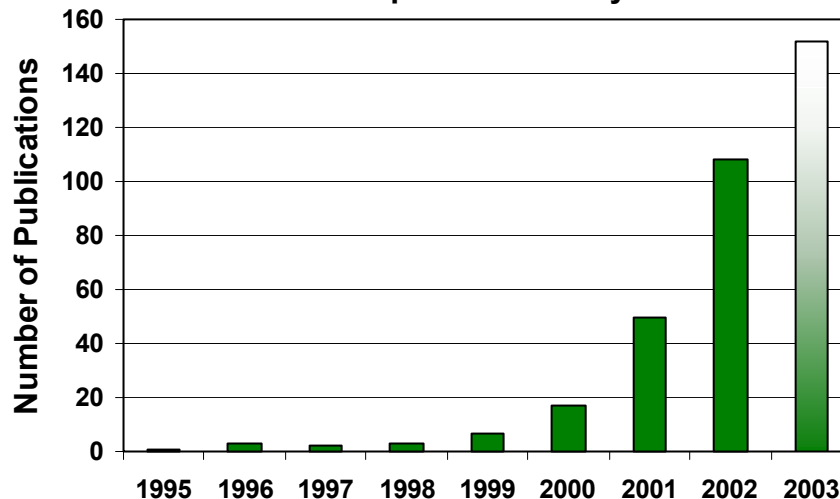
Purpose

- **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

"Ionic Liquid*" & "Catalysis"



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.

Supply

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

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TODAY'S HEADLINES

March 31, 2003

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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

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**