Ionic Liquids

A new class of solvents for chemical reactions in the future

Ennio Vanoli, Lausanne 10.11.2010
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University of Applied Sciences (HES-SO) (Chemistry and Life Sciences)
EIA-FR / Institute of Chemistry

Industrial Chemistry

Applied Chemistry
Strategic Axes of institute of chemistry

- Synthesis of fine chemical products (pharma)
- Optimization of chemical processes
- Scale up and production of chemical products
- Online analysis
What are Ionic Liquids?

- "Ionic liquids, or molten salts, are defined as materials containing only ionic species without any neutral molecules and having a low melting point (usually less than 100°C)"

Interest for the ionic liquids (literature)
Principle of IL’s synthesis

**Quaternization reaction**

\[ NR_3 \xrightarrow{R’X} [NR_3R’]^+X^- \]

1. \( M^+[A]^- \)
2. \( H^+[A]^- \)

**Anion Exchange**

\[ [NR_3R’]^+[A]^- \]
Examples of Ionic Liquids

1-butyl-3-methyl-imidazolium hexafluorophosphate

[bmim] [PF$_6$]

1-butyl-pyridinium tetrafluoroborate

[bpy] [BF$_4$]
Vapor Pressure of Ionic Liquids

- IL’s have a **small** or **not measurable vapor pressure** (very high boiling point)

- Ecological solvent

- **Advantage for the chemical process**
  (separation of synthesis products by distillation)
Miscibility of IL’s with water

By changing the nature of ions, it is possible to change the miscibility with water:

IL water
no soluble

IL water
soluble

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Multiphase Reaction in IL’s

Water

Ionic liquid

Dichloromethan
Applications of Ionic Liquids

1. Energy

2. Biotechnology

3. Chemistry

4. Industrial Chemistry
Applications of Ionic Liquids

1. Energy
   - Solar Cell
   - Battery Cells
   - Heat Storage

2. Biotechnology
   - Enzyme Catalysis
   - Protein Synthesis
   - Cellulose Chemistry
Applications of Ionic Liquids

3. Chemistry

- Heck reactions
- Suzuki Reactions
- Diels-Alder Reactions
- Friedel-Crafts
- Epoxidations
- Energetic IL

4. Industrial Chemistry

- Extraction
- Extractive Distillation
- Membrane Separation
Principle of Heck Reaction

- Heck reaction related transformation for selective C-C coupling
- Versatility for fine chemical synthesis

\[ \text{R} + \text{ArX} + \text{NET}_3 \xrightarrow{\text{Pd}} \text{R} - \text{Ar} + \text{Et}_3\text{NH}^+\text{X}^- \]

- Catalyst is very expensive

- Classical condition:
  solvent: DMF (dimethylformamid) ;
  catalyst lost after one cycle of reaction
  (formation of black palladium)
Development of New Ionic Liquid for the Heck Reaction

Step 1: Synthesis of sulfonic-ester

Step 2: Nucleophilic substitution

Objective: New IL

1-butyl-3-methyl imidazol Tosylate
[bmim] [Tosylate]
**Comparison of Heck reaction in different solvents**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Temperature [°C]</th>
<th>Time [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF a)</td>
<td>100</td>
<td>8</td>
<td>65</td>
</tr>
<tr>
<td>[bmim][PF6] b)</td>
<td>100</td>
<td>72</td>
<td>65</td>
</tr>
<tr>
<td>[bmim][Tosylate]</td>
<td>100</td>
<td>6</td>
<td>85</td>
</tr>
</tbody>
</table>

Optimization and scale up of Heck Reaction in IL

Number of cycles

Yield [%]

Heck IL Recycling of catalyst
Heck DMF Catalyst decompose
Conclusion

- Ecological solvent
- Activity and recycling of catalyst
- Miscibility
- Safety

- Price of IL
- Purity of IL
- Viscosity
Thank you for your attention