Ionic Liquids and Polymeric Solvents

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Charged substance mixtures that form a liquid at ambient temperatures.

- Unusual solvent properties (for a wide range of organic, inorganic and polymeric compounds)
- Typically consist of bulky, poorly coordinating ions
- Negligible vapor pressure – attractive alternative to VOCs
- Most Ionic Liquids are thermally stable at temp. > 200 ºC
- Wide liquid phase range (300°C)
- Very solvating, but weakly coordinating
- Immiscible with many organic solvents

- Moderate to high viscosity
- Frequently expensive, easy of separation uncertain
- Some react with water and nucleophiles
- Not necessarily innocuous
Ionic Liquids - Structure

Cations

imidazolium

pyridinium

ammonium

fosfonium

Ph-N$^+$(CH$_3$)$_3$

R-P$^+$($R'$)$_3$

tetrafluoroborate

hexafluorophosphate

heptachloroalluminate

nonaflate

BF$_4^-$

PF$_6^-$

Al$_2$Cl$_7^-$

(CF$_3$SO$_2$)$_2$N$^-$

Anions

Principle is to use large, not-symmetrical ions

– Lower lattice energy

BMIM$^+$ PF$_6^-$
General Properties of Ionic Liquids

- Choice of cation and anion determine physical properties (i.e. melting point, density, water solubility, …)
- Cations are typically big, bulky and asymmetric accounting for the low melting points
- The anion contributes more to the overall characteristics of the LI and determines the air and water stability
- Melting points can be easily changed by structural variation of one of the ions or combining different ions
- LI have low or negligible vapor pressure at 20-150°C
- Designer solvents: changing anion, the ionic liquid can adapt to specific applications.

Synthesis of Ionic Liquids

A. \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] + \[ \text{Cl} \] \[ \text{Cl} \] \[ \text{MeCN} \] \[ 60^\circ\text{C} \] \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] \[ \text{n-Bu} \] \[ \text{Cl}^{-} \] N-alkylation

B. \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] \[ \text{Cl}^{-} \] \[ \text{n-Bu} \] + \[ \text{KBF}_4 \] \[ \text{H}_2\text{O} \] \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] \[ \text{n-Bu} \] \[ \text{BF}_4^{-} \]

C. \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] \[ \text{Cl}^{-} \] \[ \text{n-Bu} \] + \[ \text{KPF}_6 \] \[ \text{H}_2\text{O} \] \[ \text{H}_3\text{C}-\text{N} \] \[ \text{N} \] \[ \text{N} \] \[ \text{n-Bu} \] \[ \text{PF}_6^{-} \] Anion exchange

Effect of Alkyl Chain Length on the Melting Point of Liquid Salts [RMIM][X]

• Most LI salts are liquid at sub-ambient temperatures.

• Are glass at low temperatures and show minimal vapour pressures until to thermal decomposition temperature (> 400°C), but some IL can be distilled at very low pressure.

• Thermal decomposition is endothermic with inorganic anions and exothermic with organic anions.

• Imidazolium cations are thermally more stable than tetraalkyl ammonium cations; the same is true for tetraalkyl phosphonium cations.

• Phosphonium cations are thermally more stable than the corresponding ammonium cations.

Using Molecular Simulations

- Detailed Geometric and Energetic model
- Adjustment of Force Field - Inter and Intermolecular Potential Functions

\[
V_{total} = \frac{1}{2} \sum_{ij} \left[ 4\sigma_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} + \frac{q_i q_j}{r_{ij}} \right] + v(\phi)
\]

\[
v(\phi) = v_3 + \frac{v_1}{2} (1 + \cos(\phi)) + \frac{v_2}{2} (1 - \cos(2\phi)) + \frac{v_3}{2} (1 + \cos(3\phi))
\]

I = Lennard Jones Plot  (includes both dispersive and electrostatic force)

Low Volume Expansivity of IL

- IL do not expand on heating as normal liquids
- Strong coulomb interactions
- IL with long alkyl chains are more compressible
- Results were confirmed with the tait equation i.e.

\[
\frac{\rho - \rho_0}{\rho} = C \ln \left( \frac{B + p}{B + p_0} \right)
\]

Which is useful for high pressure correlation

Comparison of Henry’s Constant, $\gamma^\infty$ water in ionic liquid and conventional solvents

$P_{sat} = 0.031 \text{ bar}$, Temperature = $25 \degree C$

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$[C_{8\text{min}}]_{[BF_4]}$</th>
<th>$[b_{\text{min}}]_{[PF_6]}$</th>
<th>$[C_{8\text{min}}]_{[PF_6]}$</th>
<th>Benzene</th>
<th>$\text{CCl}_4$</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>0.033</td>
<td>0.09</td>
<td>0.11</td>
<td>10</td>
<td>37</td>
<td>0.10</td>
</tr>
<tr>
<td>$\gamma^\infty$</td>
<td>2.65</td>
<td>6.94</td>
<td>8.62</td>
<td>323</td>
<td>1194</td>
<td>3.23</td>
</tr>
</tbody>
</table>
Affinity for water is greater for anions such as $[\text{BF}_4]^-\text{ than } [\text{PF}_6]^-$

Water affinity decreases with increase in alkyl length

Entropy and Enthalpy are similar like dissolution of water in short chain alcohols

Mutual solubility's increase with increase in temperature

Contamination of water creates a waste water problem - activated carbon may be the answer.

Effect of Gas Solubility

From solubility tests of nine different gases in [bmim][PF₆] was concluded:

- Carbon Dioxide: highest solubility followed by ethylene and ethane
- Argon and Oxygen showed very low solubility
- Solubility decreases with increase in temperature
- Enthalpy and Entropy changes also indicate strong molecular interactions for carbon dioxide

Comparison of Henry’s Constants (Bar)

<table>
<thead>
<tr>
<th></th>
<th>[Bmim][PF₆]</th>
<th>Heptane</th>
<th>Benzene</th>
<th>Ethanol</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.17</td>
<td>-</td>
<td>10³³</td>
<td>0.1³⁴</td>
<td>0.3³⁴</td>
</tr>
<tr>
<td>CO₂</td>
<td>53.4</td>
<td>84.3</td>
<td>104.1</td>
<td>159.2</td>
<td>54.7</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>173</td>
<td>44.2</td>
<td>82.2</td>
<td>166</td>
<td>92.9</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>355</td>
<td>31.7</td>
<td>68.1</td>
<td>148.2</td>
<td>105.2</td>
</tr>
<tr>
<td>CH₄</td>
<td>1690</td>
<td>293.4</td>
<td>487.8</td>
<td>791.6</td>
<td>552.2</td>
</tr>
</tbody>
</table>

Polarity

- Important property to determine its solvent strength
- Betaine dye was used with the help of Fluorescent tubes ($E_T$)

<table>
<thead>
<tr>
<th>Component</th>
<th>$E_T$ (30)</th>
<th>Cost (€/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Bmim}][\text{PF}_6]$</td>
<td>52.39</td>
<td>260</td>
</tr>
<tr>
<td>$[\text{C}_8\text{mim}][\text{PF}_6]$</td>
<td>46.84</td>
<td>300</td>
</tr>
<tr>
<td>$[\text{BuPy}][\text{BF}_4]$</td>
<td>44.91</td>
<td>180</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>45.30</td>
<td>10</td>
</tr>
<tr>
<td>Methanol</td>
<td>55</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Acid and Base Solutions

Reversible partitioning of Thymol Blue between water and IL
Correlation Between Partitioning in IL/Water and 1-Octanol/water Biphasic Systems

1-octanol/water Partition Coefficient (P) vs. Distribution Ratio (D) in Ionic Liquid/Water System

- Phthalic acid
- Aniline
- 4-Hydroxybenzoic acid
- Salicylic acid
- Benzoic acid
- p-Toluic acid
- Benzene
- Chlorobenzene
- Toluene
- 1,2,4-trichlorobenzene
- 1,4-dichlorobenzene
- 4,4'-dichlorodiphenol
Ionic Liquids - Uses

- Chemical Processing (solvents for catalysis)
- Pharmaceuticals
- Petroleum Refining (i.e. desulfurisation)
- Microelectronics
- Metal deposition (e.g. Aluminum)
- Organic Polymer Processing
- Pulp and Paper
- Nuclear Fuels
- Textiles
- Lubricants
- Anti-static agents
- Agents for the elimination of trace components
# Recent Applications of Ionic Liquids

<table>
<thead>
<tr>
<th>Name</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. Beckman</td>
<td>sc CO₂ Stripping after extraction</td>
</tr>
<tr>
<td>P. Bonhote</td>
<td>Conductive IL</td>
</tr>
<tr>
<td>R. Carlin</td>
<td>Ionic Liquid - polymer gel electrolytes</td>
</tr>
<tr>
<td>J. Dupont</td>
<td>Catalytic hydrogenation Reactions</td>
</tr>
<tr>
<td>C. Hussey</td>
<td>Electrochemistry in IL</td>
</tr>
<tr>
<td>H. Oliver</td>
<td>Butene dimerization</td>
</tr>
<tr>
<td>B. Osteryoung</td>
<td>Benzene polymerization</td>
</tr>
<tr>
<td>R.D. Rogers</td>
<td>Two-phase separations</td>
</tr>
<tr>
<td>K. Seddon</td>
<td>Friedel-Crafts reactions; regioselective alkylation.</td>
</tr>
<tr>
<td>T. Welton</td>
<td>Organometallic syntheses</td>
</tr>
</tbody>
</table>

### Industrial Processes with Ionic Liquids

<table>
<thead>
<tr>
<th>Company</th>
<th>Process</th>
<th>IL function</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>Acid Scavenging</td>
<td>Auxiliary</td>
<td>commercial</td>
</tr>
<tr>
<td></td>
<td>Extractive distillation</td>
<td>Extractant</td>
<td>pilot</td>
</tr>
<tr>
<td>IFP</td>
<td>Chlorination</td>
<td>Solvent</td>
<td>pilot</td>
</tr>
<tr>
<td>Degussa</td>
<td>Olefin Dimerization</td>
<td>Solvent</td>
<td>commercial</td>
</tr>
<tr>
<td></td>
<td>Hydrosilylation</td>
<td>Solvent</td>
<td>pilot</td>
</tr>
<tr>
<td></td>
<td>Compatibilizer</td>
<td>Perform. additive</td>
<td>commercial</td>
</tr>
<tr>
<td>Arkema</td>
<td>Fluorination</td>
<td>Solvent</td>
<td>pilot</td>
</tr>
<tr>
<td>Chevron Philips</td>
<td>Olefin Oligomeriz.</td>
<td>Catalyst</td>
<td>pilot</td>
</tr>
<tr>
<td>Eastman</td>
<td>Rearrangement</td>
<td>Catalyst</td>
<td>commercial</td>
</tr>
<tr>
<td>Eli Lilly</td>
<td>Cleavage of Ether</td>
<td>Catalyst/Reagent</td>
<td>pilot</td>
</tr>
<tr>
<td>Air Products</td>
<td>Storage of gases</td>
<td>Liquid Support</td>
<td>commercial</td>
</tr>
<tr>
<td>Iolitec/Wandres</td>
<td>Cleaning Fluid</td>
<td>Perform. additive</td>
<td>commercial</td>
</tr>
</tbody>
</table>
Examples of Reactions in IL

Pd(II) Compounds in [bmim][BF₄] catalyze butadiene and butene hydrodimerization.

\[
\text{butadiene} \xrightarrow{\text{Pd(II)}} \text{butadiene dimer}
\]


Product insoluble in Ionic Liquid

97% catalyst retained in IL phase
Asymmetric Catalytic Hydrogenation on Solid Support with Ionic Liquid

\[ \text{R}^1 \quad \text{H}_2 \quad \text{R}^2 \quad \text{CO}_2 \]

- **Supported Ionic Liquid Phase (SILP)**
  - Silica based support
  - Catalyst is soluble in Ionic Liquid
  - Ionic Liquid and Catalyst are fixed in the silica pores
  - Diffusion pathway is reduced

- **Catalyst**
  - Rhodium (Rh) based
  - Uses chiral Quinaphos Ligand
  - More efficient when applied in continuous flow
  - Deactivates with time

Chiral Quinaphos Ligand

Ionic Liquid
Extractive Distillation and Breaking Azeotropes

- IL have greater affinity for some components in a mixture
- Results in a change in the activity coefficients that usually enhances separation
- No IL in distillate
- Arlt claims that virtually all azeotropes can be broken by the correct selection of an ionic liquid

- Gmehling and Krummen, DE10154052
- Arlt et al., DE10136614/WO2002074718
Deep Eutectic Solvents (DES)

- DES is a fluid generally composed of two or three cheap and safe components that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component. Complex formed between a quaternary ammonium salts and a hydrogen bond donor.

- Example: $2 \text{H}_2\text{NC(=O)NH}_2 / \text{1 HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3$ (choline) or

- Example: $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}] \text{I}^- / \text{Glycerol}^*$ or urea / ethylene glycol

- **Versatile, economic, environmentally compatible, biodegradable**

Uses of Deep Eutectic Solvents

- Metal Deposition, e.g. Cr
- Electropolishing
- Ore reprocessing
- Catalysis

Wide range of solutes show high solubility e.g. metal oxides.

Melting Points of Eutectic Liquid ChCl/Urea

Comparison between Classical Solvents and Neoteric Solvents

dielectric constant

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Solutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>water (78)</td>
<td>salts</td>
</tr>
<tr>
<td>methanol (33)</td>
<td>Amino acids</td>
</tr>
<tr>
<td>ethanol (25)</td>
<td></td>
</tr>
<tr>
<td>acetone (21)</td>
<td></td>
</tr>
<tr>
<td>chloroform (4.8)</td>
<td></td>
</tr>
<tr>
<td>toluene (2.4)</td>
<td>Polar organic</td>
</tr>
<tr>
<td>CCl₄ (2.2)</td>
<td>polymers</td>
</tr>
<tr>
<td>Hexane (2)</td>
<td></td>
</tr>
</tbody>
</table>

Gas expanded Liquids

Ionic Liquids / eutectics

sc fluids
Solvent Formulations

• The most appropriate solvent may contain a variety of components depending on the solute and the application
  ▪ e.g. water, surfactants, alcohols, buffers, oils

• Formulation meets the operative functionality principle.
Polymeric /immobilized or derivatized Solvents

- Solvents that are oligomeric, polymeric, or that are tethered to polymeric systems

- Advantages:
  - Low volatility
  - No ozone depleting potential (ODP)
  - No global warming potential (GWP)
  - Possible ease of separation

- Disadvantages:
  - Expensive to manufacture
  - Life cycle impact uncertain
  - Possible separation difficulties
Derivatized/Polymeric Solvent Replacement for THF
How We can Select a Solvent

• Solvent alternatives Guide
  
  clean.rti.org/

• Solvent data base
  
  solvdb.ncms.org/index.html

• Expert systems available on web
  
  www.epa.gov/greenchemistry/tools.htm

• Environmental fate data base
  
  esc.syrres.com/efdb.htm