Ionic Liquids and Polymeric Solvents.

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Ionic Liquids (LI) – Room-Temperature Ionic Liquids (RTIL).

**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 °C
- 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

\[ \text{imidazolium} \quad \text{pyridinium} \quad \text{ammonium} \quad \text{fosfonium} \]

Ph-N^+(CH_3)_3  R-P^+(R')_3

Anions

\[ \text{tetrafluoroborate} \quad \text{hexafluorophosphate} \quad \text{heptachloroalluminate} \quad \text{nonaflate} \]

\[ \text{BF}_4^- \quad \text{PF}_6^- \quad \text{Al}_2\text{Cl}_7^- \quad (\text{CF}_3\text{SO}_2)_2\text{N}^- \]

*Principle is to use large, not-symmetrical ions*

– Lower lattice energy
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.

Rogers R.D. *Chem. Comm.* 1998. 1765-1766.
Synthesis of Ionic Liquids.

A. \( \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} + \text{Cl}^-\text{Cl} \xrightarrow{\text{MeCN}, 60^\circ\text{C}} \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} \text{Cl}^- \)  
N-alkylation

B. \( \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} + \text{KBF}_4 \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} \text{BF}_4^- \)  
Anion exchange

C. \( \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} + \text{KPF}_6 \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{C}^-\text{N}^+\text{N}^-\text{n-Bu} \text{PF}_6^- \)  
Anion exchange

Huddlestone G.J., Rogers R.D., *Green Chemistry* 2001, 3, 156-164.
Effect of Alkyl Chain Length on the Melting Point of Liquid Salts [RMIM][X].

Holbrey J.D., Seddon, K.R. J. Chem. Dalton Trans 1998,
Thermal Properties of Imidazolium Ionic Liquids.

- 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.

Ngo H.L. *Thermochimica Acta*. 2000, 357-358, 97-102.
Using Molecular Simulations.

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

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

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

\[ l = \text{Lennard Jones Plot} \quad \text{(includes both dispersive and electrostatic force)} \]

Shah. K.J, Brennecke. F.J, Magnin. E.J., *Green Chemistry*, 2002, 4, 112-116.
Low Volume Expansivity of IL.

| Volume Expansivity (K⁻¹) | Ionic Liquid | Toluene (Molecular Solvent) | Water |
|--------------------------|--------------|-----------------------------|-------|
| αₚ                       | 5-6 × 10⁻⁴   | 8-11 × 10⁻⁴                 | 2.57-5.84 × 10⁻⁴ |

- 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.

Brennecke F.J., Gu J., J. Chem. Eng. Data 2002, 47, 339-345.
Comparison of Henry’s Constant, $\gamma^\infty$ water in ionic liquid and conventional solvents.

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

| Comp. | [C$_8$min] [BF$_4$] | [bmin] [PF$_6$] | [C$_8$min] [PF$_6$] | Benzene | CCl$_4$ | Ethanol |
|-------|---------------------|-----------------|---------------------|---------|--------|---------|
| $H_1$ | 0.033               | 0.09            | 0.11                | 10      | 37     | 0.10    |
| $\gamma^\infty$ | 2.65               | 6.94            | 8.62                | 323     | 1194   | 3.23    |
(IL) Water Solutions.

- 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.

Anthony J.L., Magnin J.E., Brennecke F.J. *J.Phys.Chem. B*. **2001**, *105*, 10942-10949.
Effect of Gas Solubility.

From solubility tests of nine different gases in [bmim][PF$_6$] 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)**

|          | [Bmim][PF$_6$] | Heptane | Benzene | Ethanol | Acetone |
|----------|----------------|---------|---------|---------|---------|
| H$_2$O   | 0.17           | -       | 10$^{33}$ | 0.1$^{34}$ | 0.3$^{34}$ |
| CO$_2$   | 53.4           | 84.3    | 104.1   | 159.2   | 54.7    |
| C$_2$H$_4$ | 173           | 44.2    | 82.2    | 166     | 92.9    |
| C$_2$H$_6$ | 355           | 31.7    | 68.1    | 148.2   | 105.2   |
| CH$_4$   | 1690           | 293.4   | 487.8   | 791.6   | 552.2   |

Magnin J.E., Anthony J.L., Brennecke J.F. *J. Phy. Chem. B*. **2002**, 106,7315-7320.
Polarity.

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

| Component          | $E_T$ (30) | Cost (€/kg) |
|--------------------|------------|-------------|
| [Bmim][PF$_6$]     | 52.39      | 260         |
| [C$_8$mim][PF$_6$] | 46.84      | 300         |
| [BuPy][BF$_4$]     | 44.91      | 180         |
| Acetonitrile       | 45.30      | 10          |
| Methanol           | 55         | 0.8         |

Samanta A., Brennecke F.J. *Chem. Comm.* **2001**, 413-414.
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.

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

| Author          | Topic                                                                 |
|-----------------|----------------------------------------------------------------------|
| E. Beckman      | sc CO$_2$ Stripping after extraction                                  |
| P. Bonhote      | Conductive IL                                                        |
| R. Carlin       | Ionic Liquid - polymer gel electrolytes                               |
| J. Dupont       | Catalytic hydrogenation Reactions                                     |
| C. Hussey       | Electrochemistry in IL                                                |
| H. Oliver       | Butene dimerization                                                  |
| B. Osteryoung   | Benzene polymerization                                                |
| R.D. Rogers     | Two-phase separations                                                 |
| K. Seddon       | Friedel-Crafts reactions; regioselective alkylat.                    |
| T. Welton       | Organometallic syntheses.                                             |

P. Wasserscheid, T. Welton *Ionic Liquid in Synthesis*, Wiley Ed. 2008
## Industrial Processes with Ionic Liquids.

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

Pd(II) Compounds in [bmim][BF$_4$] catalyze butadiene and butene hydrodimerization.

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

Dupont J. Et al. *Organometallics* 1998, 17, 815

Product insoluble in Ionic Liquid

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

\[ R^1 \underbrace{\cdots} + H_2 \underset{\text{CO}_2}{\text{R}^1} \rightarrow \text{R}^1 \underbrace{\cdots} \]

**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

Inert Support
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: $2\text{H}_2\text{NC(=O)NH}_2 / 1\text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3$ (choline) or
  - Example: $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}]\Gamma / \text{Glycerol*}$ or urea / ethylene glycol.
- **Versatile, economic, environmentally compatible, biodegradable.**

*Jhong, H.R. et al. *Electroc. Comm.* 2009, 11, 209–211.*
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.

Q. Zhang, K. De Oliveira Vigier, S. Royera, F. Jérôme Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev., 2012, 41, 7108-7146
Yan Shen, Xiaoxia He, and Francisco R. Hung, Structural and Dynamical Properties of a Deep Eutectic Solvent Confined Inside a Slit Pore, J. Phys. Chem. C 2015 119 (43), 24489-24500
Melting Points of Eutectic Liquid ChCl/Urea.

\[ T_m \text{ ChCl} \]

\[ T_m \text{ Urea} \]

ChCl = Choline chloride

Rengstl D, Fischer V, Kunz W. *Phys Chem Chem Phys*. 2014 Nov 7;16(41):22815-22
Comparison between Classical Solvents and Neoteric Solvents.

- **dielectric constant**
  - 78: water
  - 33: methanol
  - 25: ethanol
  - 21: acetone
  - 4.8: chloroform
  - 2.4: toluene
  - 2.2: CCl₄
  - 2: Hexane

- **solvents**
  - Alcohols
  - Ether
  - Hydrocarbons

- **solute**
  - Salts
  - Amino acids
  - Polar organic polymers
  - Fats
  - Oils

- **Solvents Types**
  - Classical Solvents
  - Neoteric Solvents
  - 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:

\[
\text{OH} \quad + \quad \text{Cl} \quad \xrightarrow{\text{Na}} \quad \text{O} \quad \xrightarrow{70^\circ C} \quad \text{O} \\
\xrightarrow{85^\circ C} \quad \text{O} \quad \text{n}
\]
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