Greener Solvents

Dr. Tamer Andrea
Queen’s University
The Commercialization Gap

Typical stage of university technologies:
• Bench-test proof of utility
• Applications speculative and unproven
• Incomplete material characterization
• Grams of sample
• Manufacturing feasibility not studied

What Industry wants:
• Demonstrated scale-up
• Optimization
• Field-test proof of utility
• Kilograms of sample
Process for Technology Disclosures

Stage 1: Quick Screening

Stage 2: Technology Assessment

Stage 3: Technology Development

Output: analysis of commercialization potential

Assessment indicates need for PoP funding

GCC exclusive license

GCC Option

Output: licensable technology; 75/25 split

Output: technology returned without assessment
Green Solvents

Dr. Philip Jessop
Queen’s University
GOALS OF GREEN CHEMISTRY: REDUCE SOLVENT USE

“E” factor = \( \frac{\text{Mass of waste}}{\text{Mass of product}} \)

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Product tonnage</th>
<th>E factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk chemicals</td>
<td>(10^4 - 10^6)</td>
<td>(&lt;1 - 5)</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>(10^3 - 10^4)</td>
<td>(5 - 50)</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>(10 - 10^3)</td>
<td>(25 - \text{over 100})</td>
</tr>
</tbody>
</table>


Mass utilization in fine chemical production

Solvent 80-90%

Other 10-20%
Explosion, fire at Quebec plant; two; 19 more sent to hospital

SHERBROOKE, Que. — The Canadian Press
Published Thursday, Nov. 08 2012, 3:11 PM EST

Streets explode in Louisville, Kentucky
13 Feb 1981

Hexane Leak Cited for Explosions At Soybean Plant

Radio Iowa, Des Moines; Associated Press
February 2008

Barton Solvents Plant, Jul 2007
PROBLEMS WITH CURRENTLY USED SOLVENTS

In the US in the early 1990’s:
• solvent production was 26 million tons p.a.
• of tracked chemicals, many of the top chemicals released or disposed of were solvents
  (MeOH, toluene, xylene, CS₂, MEK, CH₂Cl₂)

Organic solvent hazards
• flammable (almost all except chlorinated solvents)
• carcinogenic (chlorinated solvents and aromatics)
• high vapour pressure (i.e. inhalation route)
• narcotic (ether, chloroform)
• toxic (MeOH, CS₂)
• mutagens/teratogens (toluene)
• peroxides (ethers)
• smog formation
OUTLINE

1. Reducing the Impact of Solvents
2. Solvent Properties
3. Greener Conventional Solvents
4. Unconventional Solvents
5. Conclusions
DECREASING THE IMPACT OF SOLVENTS

1. Reduce the volume of solvent
   • use higher concentrations
   • use solvent for more than one step

2. Make the solvents greener
   • carefully chosen conventional solvents
   • new green solvents
Murphy’s Law of Solvents

“The best solvent for any process step is bad for the subsequent step.”
AN IMAGINARY PROCESS

Solving Murphy’s Law of Solvents

1. A Compromise Solvent
2. A Switchable Solvent
CAREFUL SELECTION OF A TRADITIONAL SOLVENT

MeNH₂, TiCl₄

MeNH₂, EtOH

MeNH₂, TiCl₄

MeNH₂, EtOH

Pd/C

Pd/CaCO₃, EtOH

D-mandelic acid

D-mandelic acid

Sertraline

Sertraline
SWITCHABLE-POLARITY SOLVENT

\[ \text{CO}_2 \] + ROH \xrightarrow{\text{N}_2} \text{CO}_2 \text{N}_2 \text{or Ar} \]

\[ 2R_2\text{NH} \xrightarrow{\text{CO}_2} [R_2\text{NH}_2]^+ \quad \text{CO}_2 \quad \quad \text{[R}_2\text{NH}_2]^+ \quad \text{[OC(O)OR]}^- \]

Nature (2005) 436, 1102
APPLICATION TO POLYSTYRENE SYNTHESIS

1.0 mL styrene
4.5 mL DBU/PrOH
45 mg initiator

75 °C
6 h

CO₂

filter or centrifuge

$\text{Mn} = 412,000$
$\text{PDI} = 1.57$

$\text{N}_2$
DECREASING THE IMPACT OF SOLVENTS

1. Reduce the volume of solvent
   - use higher concentrations
   - use solvent for more than one step

2. Make the solvents greener
   - carefully chosen conventional solvents
   - unconventional solvents
1. Reducing the Impact of Solvents
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5. Conclusions
PROPERTIES OF CONCERN

For green-ness
boiling point / energy to distill
flash point
energy to distill
cumulative energy demand
the 10 factors

For utility
polarity
basicity / hydrogen-bond accepting ability
acidity / hydrogen-bond donating ability
viscosity
THE TOOLBOX ANALOGY

high basicity, low polarity
# Kamlet-Taft Solvatochromic Parameters

The Kamlet-Taft solvatochromic parameters describe the ability of solvents to participate in hydrogen bonding and differences in the solvent properties. These parameters are used to understand and predict solvent effects on chemical reactivity.

## Parameters
- **Acidity or proticity or H-bond donating ability**
- **Basicity or H-bond accepting ability**
- **Polarity & polarizability**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>α</th>
<th>β</th>
<th>π*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>benzene</td>
<td>0</td>
<td>0.1</td>
<td>0.59</td>
</tr>
<tr>
<td>MeCN</td>
<td>0.19</td>
<td>0.31</td>
<td>0.75</td>
</tr>
<tr>
<td>NEt₃</td>
<td>0.14</td>
<td>0.71</td>
<td>0</td>
</tr>
<tr>
<td>water</td>
<td>1.17</td>
<td>0.47</td>
<td>1.09</td>
</tr>
</tbody>
</table>

The cubic representation visualizes the solvatochromic parameters with α, β, and π* as the axes.
KAMLET-TAFT SOLVATOCHROMIC PARAMETERS

protic solvents

aprotic solvents

β (basicity)

α (acidity)

π* (polarity/polarizability)
KAMLET-TAFT SOLVATOCHROMIC PARAMETERS

protic solvents

aprotic solvents

α (acidity)

β (basicity)

π* (polarity/polarizability)

water

toluene

tBuOH

formamide

HMPA

NEt₃

cyclohexane

CHCl₃
SURVEY OF SOLVENTS (APROTIC)

Jessop, Green Chem (2012) 14, 1245
SURVEY OF SOLVENTS (PROTIC)

Jessop, Green Chem (2012) 14, 1245
OUTLINE

1. Reducing the Impact of Solvents
2. Solvent Properties
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5. Conclusions
<table>
<thead>
<tr>
<th>PFIZER SOLVENT SELECTION GUIDE</th>
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<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Acetone</td>
</tr>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>2-Propanol</td>
</tr>
<tr>
<td>1-Propanol</td>
</tr>
<tr>
<td>Heptane</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
</tr>
<tr>
<td>Isopropyl acetate</td>
</tr>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>MEK</td>
</tr>
<tr>
<td>1-Butanol</td>
</tr>
<tr>
<td>t-Butanol</td>
</tr>
<tr>
<td>Cyclohexane</td>
</tr>
<tr>
<td>Toluene</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>TBME</td>
</tr>
<tr>
<td>Isooctane</td>
</tr>
<tr>
<td>Acetonitrile</td>
</tr>
<tr>
<td>2-MeTHF</td>
</tr>
<tr>
<td>THF</td>
</tr>
<tr>
<td>Xylenes</td>
</tr>
<tr>
<td>DMSO</td>
</tr>
<tr>
<td>Acetic Acid</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>Pentane</td>
</tr>
<tr>
<td>Hexane(s)</td>
</tr>
<tr>
<td>Di-isopropyl ether</td>
</tr>
<tr>
<td>Diethyl ether</td>
</tr>
<tr>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Dichloroethane</td>
</tr>
<tr>
<td>Chloroform</td>
</tr>
<tr>
<td>NMP</td>
</tr>
<tr>
<td>DMF</td>
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<td>Pyridine</td>
</tr>
<tr>
<td>DMAc</td>
</tr>
<tr>
<td>Dioxane</td>
</tr>
<tr>
<td>Dimethoxyethane</td>
</tr>
</tbody>
</table>
WHICH SOLVENT IS GREENER?

General Comparison
• solvent impact
• solvent impact including manufacture
• energy to manufacture / cumulative energy demand

Application-Specific Comparision
• ISO LCA
ENVIRONMENTAL AND HEALTH RISKS

EHS assessment of organic solvents

Alcohols
Acetate esters
Acetonitrile
Dioxane
Formaldehyde
ENERGY REQUIREMENT FOR MANUFACTURE

Capello et al., *Green Chem* (2007) 9, 927
ENERGY REQUIREMENTS FOR A SOLVENT

How is hexane made?

oil $\xrightarrow{\text{distillation}}$ hexane

How is DMF made?

$\text{CH}_4$, $\text{H}_2\text{O}$, $\text{CO}_2$ $\xrightarrow{\text{syngas}}$ $\text{MeOH}$

$\text{NH}_3$ $\xrightarrow{-\text{H}_2\text{O}}$ $\text{NHMe}_2$

$\text{HCOOMe}$ $\xrightarrow{-\text{MeOH}}$ $\text{HCONMe}_2$
WHICH SOLVENT IS GREENER?

General Comparison
- solvent impact
- solvent impact including manufacture
- energy to manufacture / cumulative energy demand

Application-Specific Comparision
- ISO LCA

Why would this give a different result?
PROPOSED NEW GREEN ORGANIC SOLVENTS

- Ethyl lactate
  - low toxicity, biodegradable, renewable

- γ-valerolactone
  - low toxicity, biodegradable, renewable

- 2-methyltetrahydrofuran
  - renewable

- Cyclopentylmethylether
  - doesn’t form peroxides, low solubility in water
GREEN SOLVENTS (APROTIC)

Jessop, Green Chem (2012) 14, 1245
GREEN SOLVENTS (PROTIC)

OUTLINE

1. Reducing the Impact of Solvents
2. Solvent Properties
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5. Conclusions
UNCONVENTIONAL SOLVENTS

- water
- liquid polymer
- switchable solvent

- supercritical CO₂
- ionic liquid
- CO₂-expanded liquid
IN WATER

Why not water?

http://students.washington.edu/~haoli/photo_gallery/archives/olympic/

\[
\begin{align*}
\text{Br} & \quad \text{PhCHO} \quad \text{In/H}_2\text{O} \\
\text{Br} & \quad \text{Ph} \\
\text{OH} & \quad \text{Ph} \\
\text{OH} & \quad \text{Ph}
\end{align*}
\]

0.5 h
75% yield

Li, 1995
SWITCHABLE WATER

- low ionic strength
- low osmotic pressure
- good solvent for polar organics

- high ionic strength
- high osmotic pressure
- poor solvent for polar organics

**IONIC LIQUIDS**

- **NaCl**, mp 801 °C
- **NaBF$_4$**, mp 384 °C
- **[P$^i$Bu$_3$Me]O$_3$SC$_6$H$_4$Me**, mp < RT

- Nonvolatile
- Nonflammable
- Doesn’t create smog
- No inhalation hazards
BY GENERAL COMPARISON, ARE IONIC LIQUIDS GREEN?

<table>
<thead>
<tr>
<th></th>
<th>ADP</th>
<th>GWP</th>
<th>ODP</th>
<th>HTP</th>
<th>FAETP</th>
<th>MAETP</th>
<th>TETP</th>
<th>POCP</th>
<th>AP</th>
<th>EP</th>
<th>VOC</th>
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<tbody>
<tr>
<td>[Bmim][BF₄]</td>
<td>5.8E-2</td>
<td>3.5E+0</td>
<td>6.1E-7</td>
<td>6.1E-1</td>
<td>5.2E-2</td>
<td>4.4E+3</td>
<td>1.2E-2</td>
<td>4.5E-3</td>
<td>4.2E-2</td>
<td>1.8E-3</td>
<td>1.6E-2</td>
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<tr>
<td>H₂O</td>
<td>3.3E-6</td>
<td>5.7E-4</td>
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<td>1.2E-5</td>
<td>5.5E-7</td>
<td>4.5E-6</td>
<td>1.7E-7</td>
<td>1.6E-6</td>
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<tr>
<td>LPDE</td>
<td>2.6E-2</td>
<td>1.4E+0</td>
<td>3.1E-7</td>
<td>1.8E-1</td>
<td>4.5E-2</td>
<td>3.5E+2</td>
<td>6.7E-3</td>
<td>5.0E-3</td>
<td>1.2E-2</td>
<td>9.1E-4</td>
<td>1.1E-2</td>
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<tr>
<td>acetone</td>
<td>3.8E-2</td>
<td>2.0E+0</td>
<td>0.0E+0</td>
<td>2.3E-2</td>
<td>3.1E-3</td>
<td>5.4E+1</td>
<td>9.8E-4</td>
<td>4.2E-4</td>
<td>1.4E-2</td>
<td>1.6E-3</td>
<td>4.6E-3</td>
</tr>
<tr>
<td>benzene</td>
<td>3.1E-2</td>
<td>1.6E+0</td>
<td>9.4E-7</td>
<td>1.3E-1</td>
<td>2.0E-2</td>
<td>6.9E+1</td>
<td>3.8E-4</td>
<td>1.9E-3</td>
<td>1.0E-2</td>
<td>9.6E-4</td>
<td>9.1E-3</td>
</tr>
</tbody>
</table>


CHEMICAL STEPS IN SOLVENT SYNTHESIS

Liquid Polymers
Green Solvents?
LIQUID POLYMERS

SOME ORGANIC SOLVENTS ARE VOLATILE

Volatile Solvents

- flammability
- high insurance costs
- vapour losses
- smog formation
- inhalation hazards
  - toxic,
  - narcotic,
  - mutagenic,
  - carcinogenic

Nonvolatile Solvents

- no flammability
- low insurance costs
- no vapour losses
- no smog formation
- no inhalation hazards
SWITCHABLE-HYDROPHILICITY SOLVENTS

Under \( N_2 \):
- Hydrophobic solvent
- Water

Under \( CO_2 \):
- Hydrophilic solvent & water

Chemical structures:
- \( \text{Bu}_2\text{N} = \text{N} \text{Bu}_2 \)
- \( \text{Bu} \text{N} - \text{NH} + \text{N} \text{Bu}_2 \)
- \( \text{NMe}_2 \)
- \( \text{N} \text{Bu} \)

\( \text{Me}_2\text{NC}_{6}\text{H}_{13} \)
A REAL WORLD PROBLEM

hexane emissions to air in Canada (NPRI, 2007)

extract with solvent

Green Chem (2010) 12, 809
SOY EXTRACTION WITHOUT DISTILLATION

- Extract with solvent
- Extract with solvent
- Extract with solvent
- Extract with solvent
- Extract with solvent
- Extract with solvent
- Extract with solvent

Green Chem (2010) 12, 809
Green Chem (2011) 13, 619
USING A SWITCHABLE-HYDROPHILICITY SOLVENT

- Extract oil sands
- Add water & CO₂
- Oil & hydrophobic solvent
- Hydrophilic solvent & water
- Hydrophobic solvent & water
- CO₂
- Oil
OIL SANDS
1. Reducing the Impact of Solvents

2. Solvent Properties

3. Greener Conventional Solvents

4. Unconventional Solvents
   • Ionic Liquids
   • Liquid Polymers
   • Switchable Solvents
   • Gas-Expanded Liquids
   • Supercritical Fluids

5. Conclusions
EXPANSION OF LIQUIDS BY CO₂

Volumetric expansion of aprotic solvents by CO₂ at 40°C (Kordikowski, 1995)

Characteristics:
- tunable polarity
- tunable solvent properties
- lowered melting point
- improved mass transfer rates
- improved solubility of reagent gases
Expansion with CO$_2$ increases in the order:

water $<$ ionic liquid  liquid polymer $<$ protic polar $<$ aprotic polar $<$ nonpolar

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
<th>Volumetric change</th>
<th>Properties that change</th>
<th>Properties that don’t change</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Water</td>
<td>Very small</td>
<td>Acidity</td>
<td>Most</td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Hexane</td>
<td>Very large</td>
<td>All</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>III</td>
<td>Ionic liquids</td>
<td>Moderate</td>
<td>Viscosity</td>
<td>Polarity</td>
</tr>
<tr>
<td></td>
<td>Liquid polymers</td>
<td></td>
<td>Phase behaviour</td>
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</tr>
<tr>
<td></td>
<td>Crude oil</td>
<td></td>
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</tr>
</tbody>
</table>

**Viscosity of CO₂-expanded crude oil at 49 °C**

**CO\textsubscript{2} CAN TRIGGER INSOLUBILITY AND IMMISCIBILITY**

Polar solids are precipitated from solution when the solvent is expanded with CO\textsubscript{2}.

Some miscible liquids become immiscible when expanded with CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Solvent A</th>
<th>Solvent B</th>
<th>P, bar</th>
</tr>
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<tbody>
<tr>
<td>water</td>
<td>methanol</td>
<td>80</td>
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<tr>
<td>water</td>
<td>1-propanol</td>
<td>68</td>
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<tr>
<td>water</td>
<td>acetic acid</td>
<td>75</td>
</tr>
<tr>
<td>water</td>
<td>acetone</td>
<td>26</td>
</tr>
<tr>
<td>water</td>
<td>THF</td>
<td>&lt;10</td>
</tr>
<tr>
<td>water</td>
<td>1,4-dioxane</td>
<td>&lt;28</td>
</tr>
<tr>
<td>water</td>
<td>MeCN</td>
<td>&lt;19</td>
</tr>
</tbody>
</table>
OUTLINE

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   • Switchable Solvents
   • Gas-Expanded Liquids
   • Supercritical Fluids

5. Conclusions
SUPERCRITICAL CO₂
SOLUBILIZING POWER DEPENDS ON DENSITY

\[ \text{Fe}_3(\text{CO})_{12} \]
CO₂ AS A SOLVENT

Natex CO₂ decaffeination plant

DuPont fluoropolymer plant, N.C

Prep SFC (Novasep)

CO₂ dry cleaning

http://www.natex.at/album/index.htm
http://www.metropolitanmachinery.com/sail_star.htm
## scCO₂ AS A SOLVENT

<table>
<thead>
<tr>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
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<tbody>
<tr>
<td><strong>Safety</strong></td>
<td>Pressure</td>
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<tr>
<td>Nonflammable</td>
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<tr>
<td>Nontoxic</td>
<td></td>
</tr>
<tr>
<td>In-situ fire/explosion suppression</td>
<td></td>
</tr>
<tr>
<td><strong>Economics</strong></td>
<td>Pressure</td>
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<td>Free</td>
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<td><strong>Environment</strong></td>
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<tr>
<td>Recycled material</td>
<td>Pressure</td>
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<tr>
<td>No smog, ozone</td>
<td>Low solubility of some reagents</td>
</tr>
<tr>
<td>contribution</td>
<td></td>
</tr>
<tr>
<td>Naturally occurring</td>
<td></td>
</tr>
<tr>
<td><strong>Process benefits</strong></td>
<td></td>
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<tr>
<td>Rapid mass transfer</td>
<td></td>
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<tr>
<td>High solubility of reagent gases</td>
<td></td>
</tr>
<tr>
<td>Controllable solubilizing power</td>
<td></td>
</tr>
<tr>
<td>Easy to separate</td>
<td></td>
</tr>
</tbody>
</table>
OVERVIEW OF UNCONVENTIONAL GREEN SOLVENTS

- Ionic liquids
- Switchable polarity solvent
  - under air
  - under CO₂

Switchable hydrophilicity solvent
- ethanol
  - under CO₂
  - under air
- cxi acetone
- cxi MeOH
- scCO₂
- water
If the adoption of greener solvents over the next 20-30 years will reduce environmental damage from human activities, then the adoption of what class of solvents will be responsible for the greatest reduction in environmental damage?

- Bioderived solvents (glycerol, 2-methylTHF, valerolactone, etc.)
- CO\(_2\) (liquid, supercritical, expanded liquid)
- Conventional organic solvents (carefully selected)
- Ionic liquids
- Switchable solvents
- Solvent-free conditions
- Water (including liquid, superheated, supercritical, on-water)
survey results

solvents described in related papers in Green Chemistry in 2010
CONCLUSIONS

No solvent is perfectly green.

The nonconventional solvents are more exciting, but it’s the conventional ones that are greening the industry.

We’re making progress populating the map with green solvents.

*Is it really green?* Consider the solvent’s synthesis and its effect on the entire process.
CATIONS AND ANIONS

Cations

\[ \text{emim} \]
\[ \text{bmim} \]
\[ \text{hmim} \]

Anions

\[ \text{hydrophilic} \]
\[ \text{hydrophobic} \]
\[ \text{coordinating} \]
\[ \text{noncoordinating} \]

\[ \text{AlCl}_4 \]
\[ \text{Al}_2\text{Cl}_7 \]
\[ \text{Cl} \]
\[ \text{Br} \]
\[ \text{SO}_2\text{CF}_3 \]
\[ \text{O} \]
\[ \text{BF}_4 \]
\[ \text{PF}_6 \]
\[ \text{SO}_2\text{CF}_3 \]

\[ \text{NR}_4^+ \]
\[ \text{PR}_4^+ \]
GREEN SOLVENTS

- High polarity: MTHF (est.), MeTHF (est.), MTBE, CypOMe (est.), tBuOH, iPrOH, MeOH
- Low polarity: heptane

- High basicity: [bmim]BF₄, [bmim]NTf₂, [bmim]O₃SMe₄, MeOH
- Low basicity: water

- Protic: EtOH, iPrOH, BuOH, tBuOH
- Aprotic: acetone, MEK, EtOAc, γ-VL (est.), PrOH, γ-VL (est.), MTBE, CypOMe (est.)

- π*: Water (275 °C), Water (150 °C)
DISSOLVING CELLULOSE

Solvents known to dissolve cellulose:
- Strong alkali & CS₂
- Cellosolve (EtOCH₂CH₂OH)
- ZnCl₂ solution
- DMA / LiCl

Uses of IL cellulose solutions
- separation from lignin
- prep of cellulose for conversion to EtOH
- derivatization of cellulose

ELECTROCHEMISTRY AND ELECTRODEPOSITION

\[ \text{MCl}_3 + 3e^- \rightarrow \text{M} + 3\text{Cl}^- \]

Electrochemical Window at Pt = 4.7 V
Electrochemical Window at GC = 4.7 V

Trulove & Mantz, in Ionic Liquids in Synthesis