‘IONIC LIQUIDS - GREEN SOLVENTS?’

‘... Just because it is called an ionic liquid, does NOT make it green!’

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FINLAND – A STRANGE COUNTRY UP NORTH...
Finland, the land of midnight sun and Santa Claus

338,000 km² of which 70% forest

WHY IONIC LIQUIDS - DOGMA?
Growing demand for
- More environmentally benign processes
- Less toxic & volatile solvents
- Higher reaction rate (improved productivity)
- Better selectivity
- Improved economics
- Novel materials with unique properties
- Lower ecological impact factor
HISTORICAL MILESTONES

- 1st: Ethylammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ 1914
- N-ethylpyridium bromide-aluminium chloride melt (Hurley et al. 1951) – ‘chloroaluminates’
- Air & water stable ILs: Wilkes et al. 1992
- Later rapid expansion in the nr. of anions & cations
- Beginning of 21st century: Greener ILS preparation methods & greener ILS, chiral ILS, MW & US synthesis of ILS …

WHAT LIQUID IONIC AND EUTECTIC MELTS ARE?

1. CATION – ANION PAIRS
- Bulky, organic cation with delocalized charge (+)
- Smaller or bigger inorganic or organic anion (-)

2. ZWITTERIONS
- Bulky organic molecule with internal charge distribution

3. DEEP EUTECTIC MIXTURES (e.g. BINARY)
- e.g. Choline chloride-Urea
FACTS ... OR ARE THEY?

- 'Green solvents'
- Recyclable

... can be, with correct design (ester, ether alkylchains, deep eutectics, nature derived species)

... but:

many are moderately or VERY toxic, especially to aquatic organisms, bio-degradability depends on the design.

TOXIC cations (e.g. alkaloids) and anions (e.g. cyanate) are many

FACTS ... OR ARE THEY?

- Negligible vapour pressure
- Do not evaporate?

vapour pressure often in the range of $10^{-5} - 10^{-6}$ bar

... but not always:

the lower the viscosity, the more likely that there is significant vapour pressure (e.g. protonated ILS)

Some can be distilled under high vacuum, at carefully chosen temperature window:

The IL structure reorganizes upon condensation back to ionic species
FACTS … OR ARE THEY?

- Non-flammable

Yes and no, since:

many energetic ILS (oxygen and nitrogen rich molecules) ignite as fine aerosols, upon heating in oxygen atmosphere and at decomposition temperature.

- even EXPLOSIVES can be formulated!
- Shock sensitivity when notoriously dried a questionmark

Smiglak et al.

STILL FACTS, TODAY ...

- Potential formulations range to millions
- Very wide liquidus range (at best -100 to over + 400°C)
- Polar (but difficult to classify)
- Often high thermal stability
- High and unusual solvation properties (e.g. cellulose, minerals, carbohydrates can be dissolved in technically feasible concentrations)
- Non-coordinating solvents
TUNABLE PROPERTIES

- High solubilities of industrially important gases can be designed
- Sc-CO₂ has unlimited solubility in ionic liquids but ILs do NOT dissolve in sc-CO₂ (separation, precipitation, reaction aspects)
- Task-specific ILs for reversible capture of e.g. CO₂ in high amounts, ILs with para-magnetic properties, chiral ILs, catalytic ILs
- Wide electrochemical window
- ILs couple strongly with microwaves

Example: REVERSIBLE CO₂ capture and sequestration by an ionic liquid

IMPORTANT CONSIDERATIONS

- Often relatively high-viscous at room temperature but the viscosity diminishes exponentially with temperature
- Usually high molecular weights and densities somewhat under or above that of water
- Purity and humidity have a strong effect on the physico-chemical properties (e.g. halogen contamination and water for viscosity, decomposition temperature, reaction rates, …)
ILs SYNTHESIS

- So, ILs have controversial properties in terms of their 'green' image...

To begin with, let's look at a few definitions...

- How about the synthesis of them, in general?

What Green Chemistry is?

- **Green chemistry** is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.
- Environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature.
- Green chemistry seeks to reduce and prevent pollution at its source.
- The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice.
Let's progress ... ATOM ECONOMY

- Describes the conversion efficiency of a chemical process, taking into account all atoms involved
- An important concept of Green Chemistry philosophy

\[
\text{Molecular Weight of desired products} \times 100\% \div \text{Molecular Weight all products} \]

- Can be poor even if chemical yield is 100% (e.g. Canizzaro reaction)

MOTIVATION FOR RE-THINKING

- More effective use of limited raw materials, decreased emissions and waste disposal
- A continuing evolution of synthetic methods is required
- The ideal reaction would incorporate all of the atoms of the reactants
- A key goal:
  - Synthetic efficiency in transforming readily available starting materials to the final target
  - In the quest for selectivity, a second feature of efficiency is frequently overlooked; how much of the reactants end up in the final product
CLASSICAL EXAMPLES IN ORGANIC CHEMISTRY

- An alternative process that is both selective and atom economical
- [4n + 2] electron cycloaddition, represented by the Diels-Alder reaction and the aldol condensation
- Important industrial processes such as Ziegler-Natta polymerization and hydroformylation

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CHALLENGES

- An important first step in making organic reactions more environmentally benign by design requires processes that are, to a first approximation, simple additions with anything else needed only catalytically
- Since so few of the existing reactions are additions, synthesis of complex molecules requires the development of new atom-economic methodology
- E.g. ruthenium-catalyzed reactions (oxidation, reduction and C-C bonding)
WE NEED TO CONSIDER HOW MATERIALS ARE MADE

- Ionic liquids have long been hailed as the future of green chemistry - can they live up to their promise?
- Study on the safety, disposal and environmental impacts of ILs is crucial - the statement by scientists that they are green chemicals is highly debateable.
- Unknown toxicity of ILs to humans or the environment and the unexplored disposal methods for most ILs.

ILs based on imidazole and fluorinated anions are likely to be toxic and, while they cannot enter the environment by evaporation, most ILs are water soluble (at least modestly) and could easily enter the biosphere this way.

Imidazolium ions typically made by reacting an imidazole-based starting material with a linear halogenoalkane, such as an alkylhalide. Alternative anions either by reaction with salts, such as silver tetrafluoroborate for anion exchange, or metal halides such as aluminium trichloride.
DIRTY BEGINNING...

- Imidazole and halogenoalkanes come from petroleum feedstocks that are neither green nor sustainable.
- Anyhow, imidazole can be synthesized from common carbohydrate species – however, the synthesis procedure of today is far from optimal.
- Hexafluorophosphate anions are often generated using toxic silver or arsenic salts and the phosphorus is obtained electrochemically, requiring vast amounts of energy and generating much pollution.
- Chloroaluminate anions are generated using aluminium trichloride.
- We need to look at specific examples of IL use rather than generic applications.

Early Soviet poster, before the modern awareness: “The smoke of chimneys is the breath of Soviet Russia.”

DIRTY BEGINNING...

World energy demand

WE NEED TO CONSIDER HOW ENERGY-INTENSIVE INDUSTRIAL OPERATIONS ARE INCLUDING CHEMICAL TRANSFORMATIONS!
DIRTY BEGINNING...

**Future of oil economy?**

"There are no problems with oil".
Dr. V. Putin, TV interview, 2006

**TYPICAL ILs PREPARATION METHODS**

- Alkylation with alkyl halides
- Alkylation with other species (e.g. N-alkylation with alkyltriflate)
- Acid-base neutralizations
- Anion metathesis (by-product salts removed by filtration or extraction)
- ... 
- Mixing (deep eutectics)

Alkylation de Friedel-Crafts du benzène
METHODS FOR CLEANER ILs

- Solvent-free anion metathesis (Green Chem. 2007, doi:10.1039/b705745h) → Volatile halide salts formed (Green ?)
- Deep Eutectics – simply mix components
- ILs derived from natural species, e.g. pinene, amino acids and carbohydrates

WHAT CATIONS?

Selected ammonium species (quaternized)

- Thiamine derivatives
- Thiazolium derivatives
- Guadinium derivatives
- Organic aminoacid derivatives
- Glucose-derived ILs (Poletti et al., Green Chem. 9, 2007)

...but the synthesis procedures of today are not too 'Green'...
**WHAT ANIONS?**

- Carboxylate salts (acetate, mandelate, lactate, tartrate, ...)
- Nitrate (NO$_3^-$)
- Organic (amino)acids (e.g. Ohno’s group)

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**SAMPLE CASE I**

- **Scionix**: using an ionic liquid (deep eutectic) to replace chromic acid in the chromium plating industry.
- Chromium(III) chloride with choline chloride
- Reduced hazards
- Improved quality
- Increasing overall current efficiency from around 15 per cent to over 90 per cent
ILs or Deep Eutectics

- ILs can be made using simple organic halide salts and complexing agents that form a hydrogen bond.
- A wide variety can be produced using cheap, non-toxic and biodegradable starting materials.
- E.g. choline chloride and urea.

SAMPLE CASE II

- **Bioniqs**
  - Cations (+): Ethanolammonium, Bis(2-methoxyethyl)ammonium, Diethanolammonium, N,N-Dimethylethanolammonium, N-Methylidethanolammonium, etc.
  - Anions (-): Formate, Acetate, Propionate, Sulfamate, Glycolate, Pivalate, etc.
SAMPLE CASE III

- Sugar based melts
- Mix of sugar/sugar alcohol/citric acid coupled with urea and inorganic salts
- (G. Imperato et al., Green Chem. 8, 2006)

SOME RECENT DEVELOPMENTS

- Improvements to 'classical ILs synthesis methods'
- Substituted tetrafluoroborate ILs instead of ion-exchange via Meerwein reagent (trimethyloxonium tetrafluoroborate, \(\text{Me}_3\text{OBF}_4\))

\[
\begin{align*}
\text{R}^+ & + \text{Me}_3\text{OBF}_4 \rightarrow \text{R}^+ \text{Me}_3\text{OBF}_4^{-} \\
\text{R}^+ \text{Me}_3\text{OBF}_4^{-} & + \text{MgO} \rightarrow \text{R}_2\text{O} + \text{Me}_3\text{OBF}_4 + \text{MgO}
\end{align*}
\]

Just as a curiosity, a very interesting concept ... ILs as solvent & catalyst

- Some Diels-Alder reactions can be performed in ionic liquids, which may also act as catalyst.
- The ionic liquid can also be modified and fine-tuned to enhance the performance of a chemical reaction.

Sample functionalized ILs cations


NEW METHODS NEEDED

- **Simple mixing** – always a good option
- **Catalysis** – systematic methodology needs to be developed – yet to be seen!
- Green chemistry principles need to be respected.
Measures of Synthetic Efficiency for Chemical Reactions

- **Reaction Yield**
  - \( \% \text{ yield} = \frac{\text{actual quantity of products achieved}}{\text{theoretical quantity of products achievable}} \times 100 \)

- **Reaction Selectivity**
  - \( \% \text{ selectivity} = \frac{\text{yield of desired product}}{\text{amount of substrate converted}} \times 100 \)

- **Atom Economy**
  - \( \% \text{ atom economy} = \frac{\text{MWt of desired products}}{\text{MWt of all products}} \times 100 \)

**ATOM ECONOMY**

- Can be improved by:
  - Careful selection of starting materials (reactants)
  - Correct choice of catalytic system

- Often transition metal-catalyzed methods that are both selective and economical

- Is, however, only one measure upon evaluation of the ‘Greenness’ of a chemical process; other important issues are e.g. energy-economy, feedstock origin, pollution generated (amount, toxicity) and cost issues.

- In synthesis, simply which of the atoms of the reactants, for all steps, are incorporated into the desired product.
CONCLUSIONS

- Limitations of raw materials, combined with environmental concerns, necessitate our rethinking of strategies toward complex organic synthesis, including ILs.

- Despite currently existing examples, many reactions are difficult to perform selectively.

- Ultimate goal must be to construct any molecule by a series of steps in which one building block is simply added to another.

- It is a fact that we have barely begun to probe the possibilities offered by catalysis and transition metal catalysis in particular emphasizes that extraordinary opportunities exist to improve our toolbox of methodologies for improved atom economy.

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CONCLUSIONS

- Most promising routes involve:
  - Mixing
  - Catalysis

...before finishing, a short commercial brake...

- Careful selection of precursors and reaction routes

...hard work and a bit of luck is needed
... ÅBO AKADEMI UNIVERSITY, year 1640 Queen Kristina establishes 'Akademien i Åbo', the first University on Finnish soil

Industrial Ecology and Green Chemistry
... year 2007 Industrial Ecology arrives at Åbo Akademi ...
Kinetics and Catalysis Group

THANKS TO ALL COLLEAGUES AT PCC!

Thank You for Your Attention

Turku - Åbo and its archipelago