Energy Applications of Ionic Liquids

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Summer School on Green Chemistry and Sustainable Energy
July 24, 2013
• What are ILs?
  – Properties
  – Are they green?

• Applications
  – CO$_2$ capture
  – Biomass processing
  – ILs as electrolytes
  – Absorption refrigeration
What are Ionic Liquids?

- Organic salts that are liquid at temperatures around ambient
- Liquid over a wide range of temperatures; hence, can be used as solvents
- Demonstrated successes as reaction solvents (olefin dimerization, metathesis, isomerizations, Diels-Alder, Friedel-Crafts alkylations and acylations, hydrogenations, C-C coupling)
- Ionic liquids have vanishingly low vapor pressures
  - fugitive emissions not a problem
  - worker exposure less likely
  - flammability danger decreased
Ionic Liquids-Evolution

- **1980s: Chloroaluminate Ionic Liquids**
  
  1st generation


- **1990s: Air- and moisture-stable Ionic Liquids**
  
  2nd generation


- **2000s: First examples of „Task Specific Ionic Liquids”**
  
  3rd generation

Typical Ionic Liquids

1-hexyl-3-methylimidazolium \((\text{CF}_3\text{SO}_2)_2\text{N} = [\text{hmim}][\text{Tf}_2\text{N}]\)
Growth in Publications

Year

Publications


0 500 1000 1500 2000 2500 3000 3500
## Properties – Liquid Range

- Liquid over a wide range of temperatures (e.g. -70 °C – 400 °C)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_m) or (T_g) (°C)</th>
<th>(T_{decomp}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[emim][Tf(_2)N]</td>
<td>-17</td>
<td></td>
</tr>
<tr>
<td>[emmim][Tf(_2)N]</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>[pmmim][Tf(_2)N]</td>
<td>-82</td>
<td>462</td>
</tr>
<tr>
<td>[bmim][[Cl]]</td>
<td>-69</td>
<td>264</td>
</tr>
<tr>
<td>[bmim][[Br]]</td>
<td>-50</td>
<td>273</td>
</tr>
<tr>
<td>[bmim][[BF(_4)]]</td>
<td>-85</td>
<td>361</td>
</tr>
<tr>
<td>[bmim][[PF(_6)]]</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>[bmim][Tf(_2)N]</td>
<td>-2</td>
<td>422</td>
</tr>
<tr>
<td>[bmim][triflate]</td>
<td>13</td>
<td>392</td>
</tr>
<tr>
<td>[bmim][methide]</td>
<td>-65</td>
<td>413</td>
</tr>
<tr>
<td>[bmim][dca]</td>
<td>-6</td>
<td>300</td>
</tr>
<tr>
<td>[bmmim][[BF(_4)]]</td>
<td>37</td>
<td>380</td>
</tr>
<tr>
<td>[bmmim][[PF(_6)]]</td>
<td>-58</td>
<td>373</td>
</tr>
</tbody>
</table>

Lowering Melting Points

- Asymmetry
- Branching
- Poorly coordinating anions
**Viscosities**

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Viscosity / mPa s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl ether</td>
<td>0.22</td>
</tr>
<tr>
<td>Water</td>
<td>1.00</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>16</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium dicyanamide</td>
<td>21</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium tetracyanoborate</td>
<td>22</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>27</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium thiocyanate</td>
<td>38</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>38</td>
</tr>
<tr>
<td>1,2-propylene glycol</td>
<td>40</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium trifluoromethylsulfonate</td>
<td>43</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate</td>
<td>44</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium methylsulfate</td>
<td>93</td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium tetrafluoroborate</td>
<td>154</td>
</tr>
<tr>
<td>1-hexyl-3-methylimidazolium tetrafluoroborate</td>
<td>224</td>
</tr>
<tr>
<td>4-methyl-N-butylpyridinium tetrafluoroborate</td>
<td>291</td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium hexafluorophosphate</td>
<td>371</td>
</tr>
<tr>
<td>1-octyl-3-methylimidazolium tetrafluoroborate</td>
<td>468</td>
</tr>
<tr>
<td>1-butyl-2,3-dimethylimidazolium tetrafluoroborate</td>
<td>932</td>
</tr>
<tr>
<td>Glycerol</td>
<td>934</td>
</tr>
</tbody>
</table>
Viscosities

Crosthwaite et al., J. Chem. Thermodynamics, 37, 2005, 559-568
Properties Sensitive to Impurities!

- Presence of water, organics, etc. reduces viscosity, density, etc.

\[
\text{[bmim][BF}_4\text{]} \\
\text{x}_{cs}
\]

Seddon et al., Pure Appl. Chem, 2000
What Impurities?

- Water – all ILs very hygroscopic
- Added solutes (reactants, products, catalysts)
- By-products from making ILs (e.g., halides)
- Decomposition products from IL synthesis
- Hydrolysis products (e.g., HF) – don’t use PF$_6$ or BF$_4$ ILs!!!
- EtSO$_4$ hydrolyzes too

\[
\text{Step 1: } \quad \text{imidazolium} + R_1 \text{Cl} \quad \xrightarrow{\text{Step 1}} \quad \text{imidazolium} \quad + \text{Cl}^{-}
\]

\[
\text{Step 2: } \quad \text{imidazolium} \quad \text{Cl}^{-} \quad + \quad \text{HX (or MX)} \quad \xrightarrow{\text{Step 2}} \quad \text{imidazolium} \quad \text{X}^{-} \quad + \quad \text{HCl (or MCl)}
\]
• Ability to dissolve polar, nonpolar and aromatic compounds
• ‘Tunable’ solubility
Are ILs Green?

- Nonvolatile, will not cause air pollution
- Dissolve in water; what is toxicity to aquatic organisms?
- Biodegradability?
- Bioaccumulation? Generally, NO; very small $K_{OW}$
- Non-mutagenic
• Can make extremely toxic or NOT
• Can’t classify ILs as a group
• \([\text{emim}][\text{EtSO}_4]\) approved in Europe under REACH
  – Hydrolyzes to \([\text{emim}][\text{HSO}_4]\) + ethanol

<table>
<thead>
<tr>
<th></th>
<th>BMIM Cl(^1)</th>
<th>EMIM EtOSO(_3)(^2)</th>
<th>MTEOA MeOSO(_3)(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute oral toxicity</td>
<td>toxic</td>
<td>not harmful</td>
<td>not harmful</td>
</tr>
<tr>
<td>Skin irritation</td>
<td>irritant</td>
<td>non-irritant</td>
<td>non-irritant</td>
</tr>
<tr>
<td>Eye irritation</td>
<td>irritant</td>
<td>non-irritant</td>
<td>non-irritant</td>
</tr>
<tr>
<td>Sensitization</td>
<td>non-sensitizing</td>
<td>non-sensitizing</td>
<td>non-sensitizing</td>
</tr>
<tr>
<td>Mutagenicity</td>
<td>non-mutagenic</td>
<td>non-mutagenic</td>
<td>non-mutagenic</td>
</tr>
<tr>
<td>Biological degradability</td>
<td>not readily degradable</td>
<td>not readily degradable</td>
<td>readily biodegradable</td>
</tr>
<tr>
<td>Toxicity to daphniae</td>
<td>acute toxic</td>
<td>acutely not harmful</td>
<td>acutely not harmful</td>
</tr>
<tr>
<td>Toxicity to fish</td>
<td>acutely not harmful</td>
<td>-</td>
<td>acutely not harmful</td>
</tr>
</tbody>
</table>

\(^1\) BMIM Cl = 1-Butyl-3-methylimidazolium chloride  
\(^2\) EMIM EtOSO\(_3\) = 1-Ethyl-3-methylimidazolium ethylsulfate  
\(^3\) MTEOA MeOSO\(_3\) = Tris-(2-hydroxyethyl)-methylammonium methylsulfate

M. Maase - BASF
Toxicity and Biodegradability

- Low toxicity to aquatic organisms
  - Cation NOT biodegradable

- High toxicity to aquatic organisms
  - Cation NOT biodegradable

Quaternary ammonium and pyridinium cations can be biodegradable; phosphonium and imidazoliums generally NOT
CO$_2$ Capture - McKinsey Conclusions

• Lots of opportunities for GHG reductions from efficiency improvements
• Energy efficiency SAVES $$\$$, even considering the capital investment
• Can’t meet target (reduce current CO$_2$ emissions by $\frac{1}{2}$) without **Carbon Capture and Sequestration (CCS)**
Post-Combustion Capture
Conventional PC Power Plant

Atmospheric pressure
~12% CO$_2$

http://www.bellona.org/factsheets/1191913555.13
Pre-Combustion Capture - IGCC

>20 atmospheres
>30% CO₂
US Dept. of Energy CCS Targets

- **Separation and Capture**
  - >50% of electricity from conventional coal in U.S.
  - Need low energy and cost post-combustion capture technology
  - Target is ~35% increase in cost of electricity

- **Sequestration/Storage**

- **Monitoring, Mitigation and Verification**
Carbon Capture & Sequestration

- Existing technology (dilute aqueous amines) impractical
  - Monoethanolamine (MEA)
  - High parasitic energy load (~28%; 80% increase in COE)
    - Large heat of reaction
    - Energy lost in evaporation of water
  - Corrosive, side reactions
  - Degrades at low temperatures
- Alternative – Ionic Liquids
Key Properties for CO$_2$ Capture

- High CO$_2$ solubility
- High CO$_2$ selectivity
- Ease of regeneration
  - Low enthalpy of solution
  - Low solubility with water
  - Low heat capacity
- Stability
  - Thermal
  - Other gases (e.g., SO$_2$)
- Low viscosity
- Inexpensive
Process Configuration

Low $T$ absorber
- Input: $CO_2$/diluent mixture
- Process: Absorption of $CO_2$
- Output: $CO_2$-rich liquid

High $T$ stripper
- Input: $CO_2$
- Process: Stripping of $CO_2$
- Output: $CO_2$-poor liquid

Graph:
- X-axis: Pressure (arbitrary units)
- Y-axis: Dissolved $CO_2$
- Low $T$ curve
- High $T$ curve
Pure Gas Solubility - CO$_2$

- Gas solubility
  - solubility $\uparrow$ pressure $\uparrow$
  - solubility $\downarrow$ temperature $\uparrow$

- Important for reusability of ILs
  - Absorb at low T
  - Remove at high T

- Trend seen for CO$_2$ solubility in all ILs measured

Muldoon, et al., JPC B, 2007, 111, 9001-9009
Pure Gas Solubility – Other gases

- Gas solubility measured in [hmpy][Tf₂N]
  - Similar trends are seen with other ILs
- CO₂ has the highest solubility of the gases measured
- Good selectivity!

Anderson, et al., ACR, 2007, 40, 1208-1216
Limitations of Physical Absorption

- Physical solubility
  - Low heat of absorption
  - Around 12 kJ/mol by temperature dependence of isotherms and direct calorimetric measurements
  - Low regeneration energy
  - Large IL circulation rates
  - Desorption at low P increases compression costs
  - Would need ~10x increase in solubility to beat aqueous MEA

- Chemical complexation
  - Strong enough to increase capacity and decrease IL circulation rates
  - Weak enough to keep regeneration energies (and temperatures) down
Chemical Complexation with ILs

• Known chemistry – add amine to IL to react with CO$_2$

\[\text{O} = \text{C} = \text{O} \quad \overset{\text{N-N}}{\text{N-H}} \quad \overset{\text{2 Tf$_2$N}^-}{\text{H}_2\text{N}} \quad \overset{\text{2 Tf$_2$N}^-}{\text{2 Tf$_2$N}^-} \quad \overset{\text{N-N}}{\text{N-H}} \quad \overset{\text{N-N}}{\text{N-H}} \quad \overset{\text{O}}{\text{O}}\]

• “Task Specific Ionic Liquids”

• Much higher capacity for CO$_2$

• Same mechanism as amines

• CO$_2$ binds with two ILs; 1:2 mechanism

Designing ILs for 1:1 binding

Mindrup and Schneider, ACS Symp. Series 2010
• Close to 1 mole $\text{CO}_2$/mole IL absorbed
• Curves level out at the same point between different batches
• Increased noise at higher pressures

Goodrich et al., JPC B, DOI: 10.1021/jp2015534
Effect of CO$_2$ on Viscosities

Goodrich et al., JPC B, DOI: 10.1021/jp2015534
Modeling of CO$_2$ Uptake

CO$_2$(g) $\rightleftharpoons$ CO$_2$(phys)

CO$_2$(phys) + IL $\rightleftharpoons$ IL-CO$_2$

**Variables**
- $z =$ Mole Ratio, moles CO$_2$ / moles IL
- $P =$ Pressure

**Parameters**
- Henry’s Law describes Physical Absorption
- $K =$ Equilibrium Constant for Chemical Absorption
- $C =$ activation sites / moles IL

$$z = \frac{P}{h} + \frac{K \cdot C \cdot P}{1 + K \cdot P}$$

Goodrich et al., JPC B, DOI: 10.1021/jp2015534
### Heat of Absorption

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$\Delta H$, kJ/mol$_{\text{CO}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{P}_{66614}][\text{Prolinate}]$</td>
<td>-80</td>
</tr>
<tr>
<td>$[\text{P}_{66614}][\text{Methioninate}]$</td>
<td>-64</td>
</tr>
</tbody>
</table>

Process simulation used to evaluate the sensitivity of a representative 500 MW coal plant CO\textsubscript{2} capture process to ionic liquid properties

Results will be used to guide the development of next-generation ionic liquids

Requirements
- Set flue gas inlet T, P and composition
- 90% CO\textsubscript{2} removal
- Adjust regenerator T and P to minimize energy needs

Sensitivity variables
- Stoichiometry
- Enthalpy of reaction
- Loading (Keq)
- Water miscibility
Different Aprotic Heterocyclic Anions

- Retain amine in ring structure but further reduce free hydrogens

pyrrolides

-80°C < T_g < -65°C

260°C < T_decomp < 330°C
AHA CO₂ Uptake

Mole ratio: CO₂/IL

Pressure (mbar)

- Indazole
- Bnim
- Pyrazole
- Brbnim
- CNpyr
- CF3pyra
- BnimSCH3
- CF3pyraCH3
- 1,2,4-Triaz
- 1,2,3-Triaz
AHA Viscosities

Very small viscosity increase when saturated with \( \text{CO}_2 \) at 1 bar and 22 °C

Gurkan et al., JPC Lett, 2010
Path Forward for CO$_2$ Capture with ILs

- Tested in lab-scale unit (4 in. columns) both at Notre Dame and Babcocks & Wilcox
- Using [P$_{66614}$][2-cyanopyrrolide]
- 25 liters from Koei Chemicals
- $\Delta H_{\text{chem}}$ lower than optimal (-43 kJ/mole)
- Continue development and testing of new AHA ILs

*Figure 1: Image of the lab-scale unit constructed for Task 18.*
Starch: 70-75% (Corn)
• Readily hydrolysable
• Basis for existing biorefineries
• Easily separable and fermentable fuels & chemicals

Oil: 4-7% (Corn) 18-20% (Soybeans)
• Readily separable from feedstock
• Starting material for clean Biodiesel
• Readily converted via chemical routes

Protein: 20-25% (Corn) 80% (Soybean Meal)
• Mostly used as a feed
• Underutilized as a polymer building block
• Potential feedstock for chemicals and resins
**Biomass Chemistry**

Lignin: 15-25%
- Complex aromatic structure
- Resists biochemical conversion
- Requires high temperatures to convert

Hemicellulose: 23-32%
- Polymer of 5- and 6-carbon sugars
- Easily depolymerization
- 5-carbon sugars hard to metabolize

Cellulose: 38-50%
- Polymer of glucose
- Susceptible to enzymatic attack
- Glucose easy to metabolize
Use of Biomass

- Use starch, oil and protein for food
- Burn lignan to generate heat and power
- Use cellulose (and maybe hemi-cellulose) for chemicals and fuel
- Need to separate the components
- Use enzymes to convert the cellulose
Processing of Biomass with Ionic Liquids

- Cellulose doesn’t dissolve in water or common organic solvents
- Cellulases must attack solid matrix
- Mass transfer limitations
- Solvents to dissolve
  - dimethylacetamide (DMAC)/LiCl solvents
  - N-methylmorpholine-N-oxide (NMNO) and phosphoric acid
  - Ionic liquids
**Dissolution of Cellulose with Ionic Liquids**

Richard P. Swatloski, Scott K. Spear, John D. Holbrey, and Robin D. Rogers*

*Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487*

Received February 1, 2002

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**Table 1.** Solubility of Dissolving Pulp Cellulose in Ionic Liquids

<table>
<thead>
<tr>
<th>ionic liquid</th>
<th>method</th>
<th>solubility (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim]Cl</td>
<td>heat (100 °C)</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>(70 °C)</td>
<td>3%</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>heat (80 °C) + sonication</td>
<td>5%</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>microwave heating</td>
<td>25%, clear</td>
</tr>
<tr>
<td></td>
<td>3–5-s pulses</td>
<td>viscous solution</td>
</tr>
<tr>
<td>[C₄mim]Br</td>
<td>microwave</td>
<td>5–7%</td>
</tr>
<tr>
<td>[C₄mim]SCN</td>
<td>microwave</td>
<td>5–7%</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>microwave</td>
<td>insoluble</td>
</tr>
<tr>
<td>[C₄mim][PF₆]</td>
<td>microwave</td>
<td>insoluble</td>
</tr>
<tr>
<td>[C₆mim]Cl</td>
<td>heat (100 °C)</td>
<td>5%</td>
</tr>
<tr>
<td>[C₈mim]Cl</td>
<td>heat (100 °C)</td>
<td>slightly soluble</td>
</tr>
</tbody>
</table>
Processing of Biomass in Ionic Liquids

- IL/biomass solutions VERY viscous
- Most cellulases inactive in ILs that dissolve cellulose
- Can reconstitute cellulose by adding antisolvents (e.g., water, acetone)
- Pretreatment methods
  - Acids, ammonia, hot water, lime
  - Explosive decompression, ammonia fiber explosion
  - Ionic liquids
Processing of Biomass with Ionic Liquids

Visualisation of Biomass Solubilization and Cellulose Regeneration During Ionic Liquid Pretreatment of Switchgrass

Seema Singh, Blake A. Simmons, Kenneth P. Vogel

-emim[acetate] disrupts/solubilized plant cell wall
- breaks up hydrogen bonding
- regenerate cellulose by adding water as an anti-solvent
- regenerated cellulose easily processed by cellulases (15x kinetics vs. untreated)
ILs as Electrolytes
Batteries, Supercapacitors, Fuel Cells

- Wide electrochemical window (up to 4-6 V)
- Can get larger voltages than you can get with an aqueous solution
- Need high conductivity

Electrolysis of water

Anode (oxidation): $2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4\text{e}^- \quad E_{\text{ox}}^o = -1.23 \text{ V}$
Cathode (reduction): $2 \text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g) \quad E_{\text{red}}^o = 0.00 \text{ V}$
Dye Sensitized Solar Cells

- Dye sensitized solar cells
- Developed by Michael Gratzel in 1991
- Molecular dye on TiO$_2$ absorbs sunlight
- Electrons flow through TiO$_2$ to electrode
- Electrons power external load
- Electrons reintroduced to cell through counter electrode
- Electrons flow through electrolyte back to dye, through iodide/tri-iodide couple
Review

Dye-sensitized solar cells

Michael Grätzel*

Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Received 3 June 2003; received in revised form 1 July 2003; accepted 1 July 2003

Abstract

The dye-sensitized solar cells (DSC) provides a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor assume both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight. Nearly quantitative conversion of incident photon into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM 1.5) to current conversion efficiencies (IPCE) over 10% have been reached. There are good prospects to produce these cells at lower cost than conventional devices. Here we present the current state of the field, discuss new concepts of the dye-sensitized nanocrystalline solar cell (DSC) including heterojunction variants and analyze the perspectives for the future development of the technology.

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Keywords: Solar light energy conversion; Dye-sensitized solar cells; Nanocrystalline oxide semiconductor films; Organic hole conductors; Ionic liquids; Ruthenium charge transfer sensitizers
Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts

Pierre Bonhôte,* Ana-Paula Dias, Nicholas Papageorgiou, Kuppuswamy Kalyanasundaram, and Michael Grätzel*

Institut de chimie physique, Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Received August 15, 1995

New, hydrophobic ionic liquids with low melting points (≤−30 °C to ambient temperature) have been synthesized and investigated, based on 1,3-dialkyl imidazolium cations and hydrophobic anions. Other imidazolium molten salts with hydrophilic anions and thus water-soluble are also described. The molten salts were characterized by NMR and elemental analysis. Their density, melting point, viscosity, conductivity, refractive index, electrochemical window, thermal stability, and miscibility with water and organic solvents were determined. The influence of the alkyl substituents in 1, 2, 3, and 4(5)-positions on these properties was scrutinized. Viscosities as low as 35 cP (for 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide (bis(triflyl)amide) and trifluoroacetate) and conductivities as high as 9.6 mS/cm were obtained. Photophysical probe studies were carried out to establish more precisely the solvent properties of 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide. The hydrophobic molten salts are promising solvents for electrochemical, photovoltaic, and synthetic applications.
Ionic Liquids as absorbent in chillers

Absorption chillers with cooling capacities of over 30MW need over 100t of absorbent. Today LiBr is used as absorbent, but it has serious technical limitations. ILs show similar thermodynamic behaviour and could resolve tech problems. It might be possible to convert heat directly into refrigeration even in very hot climates.

P. Schwab - Degussa
Absorption Refrigeration

• Replace electrical energy with low value heat energy
• Problems with conventional systems
  – LiBr/water is corrosive, solidification problems
  – Water/ammonia is toxic, odor nuisance
• Replace with IL/water, IL/CO$_2$, IL/HFC systems
Coefficient of Performance

- COP = chilling capacity/(work+heat in)
- COPs much lower for absorption refrigeration systems than vapor compression systems but lower grade energy (heat instead of electricity)
- COPs depend on enthalpies at each place in cycle
- $H$ as function of $T$, $P$ and composition
- Measure $C_p$ of pure ILs, $\Delta H_{\text{mixing}}$ of IL/water, VLE

\[ P = x_i \gamma_i P_i^{\text{sat}} \]
Absorption Refrigeration

- Excellent coefficients of performance, especially for generation temperatures < 150 °C

\[ T_{evap} = 5 \, ^\circ C \]
\[ T_{cond} = 50 \, ^\circ C \]
\[ T_{abs} = 40 \, ^\circ C \]
Summary

- ILs finding many uses in diverse energy applications
- CO$_2$ capture
- Biomass processing
  - Dissolution/pretreatment of cellulose
- ILs as electrolytes
  - Batteries, Supercapacitors, Fuel Cells, DSSC
  - Heat transfer fluid for solar thermal
- Absorption refrigeration
- Tunable nature is what is important – not one, but many different solvents