Ionic Liquids for Post-Combustion \( \text{CO}_2 \) Capture

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Outline

• Background
• Physical solubility of gases in ILs
• Chemical complexation of ILs with CO$_2$
  • Doubling capacity
  • Eliminating viscosity increase
  • Tuning reaction enthalpy
  • Details on reaction chemistry
• Phase change ionic liquids
• Conclusions
Ionic Liquids

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali salts
- Many favorable properties
  - **Nonvolatile**
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity

Examples of cations

Examples of anions
Ionic Liquids

Table salt
NaCl
\( T_m = 1474 \, ^\circ\text{F} \) (801 \(^\circ\text{C}\))

Ionic Liquid
\( T_m << \) room temperature
My Research Group

- Design, synthesis and purification of new ILs
- Thermophysical properties
  - Melting points, decomposition temperatures, viscosities, densities, ionic conductivities
  - Excess enthalpies
- Phase behavior
  - Gas solubilities, VLE, LLE, SLE
- Electrochemical properties
  - Electrochemical windows, electrochemical reduction of CO$_2$, electroplating
- Reactivity (with CO$_2$)
- Macroscopic thermodynamic modeling
Energy Applications of Ionic Liquids

• **Separations**
  - Gas separations *(CO₂ capture)*
  - Breaking azeotropes
  - Organics from fermentation broths

• **Cooling and Heating**
  - Absorption cooling
  - Co-fluid vapor-compression refrigeration and heat pumps

• **Electrolytes**
  - Batteries
  - Fuel cells
  - Supercapacitors
  - Dye sensitized solar cells

• **Biomass Processing**

• **Heat Transfer Fluids**
Important CO$_2$ Separations

- CO$_2$ from natural gas
- CO$_2$ from air
- Pre-combustion gases
- Post-combustion flue gas
CO₂ Capture

- 85% of primary energy from burning of fossil fuels
- > 50% of electricity generation from coal (more from NG)
- Point sources like power plant good targets for CO₂ capture
- Need lower energy processes for removal of CO₂ from post-combustion flue gas
- Commercial options - dilute aqueous amine solutions
  - Primarily, monoethanolamine (MEA)
  - High parasitic energy load (~28%)
  - Corrosive, side reactions
  - Degrades at low temperatures
- Alternative – ionic liquids
Post-Combustion Flue Gas

Atmospheric pressure
~12% CO₂

http://www.bellona.org/factsheets/1191913555.13
- no detectable IL in CO$_2$ phase at 40°C and 13.8 MPa
- significant solubility of CO$_2$ in IL
- 1.3-7.2 mole % IL mixtures
  immiscible at 40 MPa

Blanchard , Hancu, Beckman and Brennecke., *Nature*, May 6, 1999
Physical Dissolution of CO₂

- 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 CO₂ solubility in all ILs measured

Muldoon, et al., JPC B, 2007, 111, 9001-9009

Mark Muldoon
Physical Dissolution of Gases in ILs

- Selectivity of CO₂ over N₂, O₂, etc. is good even for physical dissolution of CO₂ in ILs.

Anderson, et al., ACR, 40, 2007, 1208-1216

Jessica (Anderson) Kuczenski
Need Chemical Complexation with CO$_2$
Low partial pressures for post-combustion

- **Physical solubility**
  - Low heat of absorption
  - $\sim -12$ kJ/mol by T dependence of isotherms and direct calorimetric measurements
  - Low regeneration energy
  - Large IL circulation rates
  - Desorption at low P increases compression costs
  - Would need $\sim10x$ 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
Build on Amine Chemistry

- Results in 1:2 CO₂ to IL molar uptake
- Huge increase in viscosity
Can We Get Higher Capacity Than 1:2?

Reaction energies in kcal/mol relative to MEA

- Local cation tethering favors 1:2 binding
- Local anion tethering disfavors 1:2 binding
- Tethering ion and tethering point as important as functional groups in controlling CO$_2$ reactions

Mindrup and Schneider, ACS Symp. Series 2010
1:1 Uptake with Amine on Anion
Forms carbamic acid, not carbamate

Large viscosity increase upon reaction with CO$_2$

[Brett Goodrich]

Goodrich et al., JPC B, 2011, 115, 9140
Effect of CO₂ on Viscosity

Goodrich et al., JPC B, 2011, 115, 9140
Effect of CO\textsubscript{2} on Viscosities

![Chemical structures of different amino acids]

- Lysinate
- Isoleucinate
- Sarcosinate
- Methioninate
- Taurinate
- Glycinate
- Prolinate

Decreasing CO\textsubscript{2} Saturated Viscosity

- Viscosity Increases with CO\textsubscript{2} because of the formation of a hydrogen bonding network.
- Prolinate, due to its ringed structure, has the least amount of free hydrogens able to participate in hydrogen bonding.

AHA – aprotic heterocyclic anions

- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding

![Graph showing mol CO₂ / mol IL vs Pressure (bar)]

Burcu Gurkan

Gurkan et al., JPC Lett, 2010
Eliminate Viscosity Increase by Using AHA – aprotic heterocyclic anions

\[ \text{C}_6\text{H}_{13}^+\text{P-C}_{14}\text{H}_{29} \]

\[ \text{N} = \text{C} = \text{N} \]

\[ \text{C}_6\text{H}_{13}^+\text{P-C}_{14}\text{H}_{29} \]

\[ \text{N} \]

\[ \text{CF}_3 \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{C}_6\text{H}_{13}^+\text{P-C}_{14}\text{H}_{29} \]

\[ \text{N} \]

\[ \text{CF}_3 \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{C}_6\text{H}_{13}^+\text{P-C}_{14}\text{H}_{29} \]

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\[ \text{N} \]

\[ \text{CF}_3 \]

\[ \text{N} \]

\[ \text{N} \]
AHA CO$_2$ Uptake as Function of $T$

\[ \Delta H_{\text{phys}} = -10 \text{ kJ/mole CO}_2 \]
\[ \Delta H_{\text{chem}} = -43 \text{ kJ/mole CO}_2 \]

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(\text{phys}) \\
\text{CO}_2(g) + \text{IL} & \rightleftharpoons \text{IL-CO}_2 \\
\end{align*}
\]

\[
Z = \frac{P_{\text{CO}_2}/H}{1 - P_{\text{CO}_2}/H} + \frac{k_1 P_{\text{CO}_2} C_3}{1 + k_1 P_{\text{CO}_2}}
\]

Gurkan et al., JPC Lett, 2010
Different Aprotic Heterocyclic Anions

Adjust $\Delta H_{chem}$ with electron withdrawing groups

pyrrololides

imidazololides

pyrazololides

triazololides
Tuning Reaction Enthalpy of AHA ILs

ΔHrxn (kJ/mol)

22 °C

[Inda] -54
[BnIm] -52
[6-BrBnIm] -48
[2-SCH₃BnIm] -41
[2-CNPyra] -45
[3-CNPyra] -44
[3-CF₃Pyra] -41
[3-CH₃,5-CF₃Pyra] -37
[3-Triaz] -42
[4-Triaz] -42

Mole CO₂/mole IL

Pressure (bar)

Seo et al., JPC B, 2014, 118, 5740

Sam Seo
Phosphonium Ylide Formation

- At room temperature carbamate salt is formed and cation is inert:

\[
\text{CN}^+\text{CN}^- + \text{CO}_2 \rightarrow \text{CN}^+\text{CN}^-
\]

- Increasing reaction temperature leads to formation of a phosphonium ylide in the presence of CO\(_2\) due to apparent acidity of the proton on the \(\alpha\)-carbon\(^a\):

\[
\begin{array}{c}
\text{[R}_1\text{R}_2\text{H}] \\
\text{R}_1\text{R}_2
\end{array}
\rightarrow
\begin{array}{c}
\text{[R}_1\text{R}_2\text{H}] \\
\text{R}_1\text{R}_2
\end{array}
\]

- At 60°C all AHA ionic liquids studied react CO\(_2\) with cation
  - 2-CNpyr at 60°C showed significant reaction with cation even though at the temperatures of the rate experiments it was not prevalent.
  - Similar mechanism to formation of carbene in imidazolium ILs\(^b,c\)

\(^b\) Gurau G. et. al. Angew. Chem. Int. 2011
CO₂ Reacts with Cation and Anion

- 2 reactions are taking place in parallel at higher temperatures
  - At low temperatures reaction 2 is kinetically limited
- Both reactions are reversible

(1)

(2)

Thomas Gohndrone
In-Situ ATR FTIR for $P_{xxxx}$ 2-CNpyr

- IR spectrum different when reaction occurs at 22°C and 60°C
  - 2 different carboxylic group stretching peaks after reaction at 60°C
  - Seen with different size cations as well
- Need to characterize the different products formed
The anion-CO$_2$ is desorbed faster than the cation-CO$_2$ during the stripping process
- Desorb under vacuum at 60°C
- Process is fully reversible
**$^{31}$P NMR for $[\text{P}_{66614}][\text{2-CNpyr}]$**

- IL reacted with CO$_2$ at 22°C
  - Same as neat IL

All samples have ~1-1.5\% of methylated impurity at 39 ppm

- IL reacted with CO$_2$ at 60°C
  - Additional peak at 32.5 ppm shows evidence of P-C coupling
  - After vacuum/desorption peak at 32.5 ppm is no longer present
NMR and FTIR Consistent

CNpyr at 40 °C

CNpyr at 60 °C
Heteronuclear Multiple Bond Correlation shows 2-3 bond C-H coupling
- New $^1$H Peak at 2.77 (phosphonium H region)
- New $^{13}$C peak at 166 ppm
- They are coupled

Evidence that CO$_2$ is in fact bound to the cation

Labeling CO$_2$ with $^{13}$C increases the intensity of CO$_2$ C-H coupling
Positive mode electron mass spec of Phosphonium IL-CO$_2$ complex.

- P$_{66614}$ Molecular Weight = 483.5
- P$_{66614}$ + $^{13}$C labeled CO$_2$ = 528.5
Replacing the phosphonium cation with ammonium eliminates ylide formation

- Phosphonium ylide is more stable than ammonium
- No change in CO₂ uptake due to the reaction with cation

Butyl-Methyl-Piperidinium [PI₁₄]

Absorption at 60°C
Discovery of Phase Change Ionic Liquids

All $T_m > 45 \, ^\circ C$

Remained liquid at 22 °C with 1 bar CO$_2$ pressure

$T_m$, complex $< T_m$, unreacted
CO₂ Capture with Phase Change Material

Absorbent goes from solid to liquid when reacts with CO₂, absorbing heat

‘Melting’ of absorbent reduces cooling duty

Heat duty in stripper reduced by the heat of fusion of the phase change material

Absorbent goes from liquid to solid when releases CO₂, releasing heat

Absorbent goes from flue gas to cleaned flue gas in absorber
CO₂ Capture with Phase Change Material

**Absorber**

- Remove 50 kJ/mol
- \([\text{C}^+][\text{A}^-] \text{(s)} + \text{CO}_2 \rightarrow [\text{C}^+][\text{ACO}_2^-] \text{(s)}] \text{ exothermic}\)
- \([\text{C}^+][\text{ACO}_2^-] \text{(s)} \rightarrow [\text{C}^+][\text{ACO}_2^-] \text{(l)}] \text{ endothermic}\)
- Add 20 kJ/mol

**Q_{net} = Remove 30 kJ/mol**

**Regenerator**

- Add 50 kJ/mol
- \([\text{C}^+][\text{ACO}_2^-] \text{(l)} \rightarrow [\text{C}^+][\text{A}^-] \text{(l)} + \text{CO}_2] \text{ endothermic}\)
- \([\text{C}^+][\text{A}^-] \text{(l)} \rightarrow [\text{C}^+][\text{A}^-] \text{(s)}] \text{ exothermic}\)
- Remove 20 kJ/mol

**Q_{net} = Add 30 kJ/mol**
Phase Change Ionic Material

70 °C

Pure material; $T_m=166$ °C; no CO$_2$

60 mbar CO$_2$

100 mbar CO$_2$

150 mbar CO$_2$
CO₂ Uptake Curves

![Graph of CO₂ solubility vs. pressure at different temperatures, showing curves for 60 °C, 70 °C, and 80 °C.]

Tₘ = 166 °C
Δh₉₄us = -19.9 kJ/mole
Δh₉₄chem = -52 kJ/mole

Seo et al., Energy & Fuels, 2014, 28, 5968-5977
Typical PCIL isotherms for idealized model, for the parameter values $\Delta H_{\text{fus}} = -20 \text{ kJ mol}^{-1}$, $T_{m,1} = 100 \degree \text{C}$, $\Delta H_{\text{rxn}} = -50 \text{ kJ mol}^{-1}$, $\Delta S_{\text{rxn}} = -130 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H_{\text{phys}} = -13 \text{ kJ mol}^{-1}$, $\Delta S_{\text{phys}} = -73 \text{ J mol}^{-1} \text{ K}^{-1}$.

Seo et al., *Energy & Fuels*, 2014, 28, 5968-5977
Figure 5. Process flow diagram for CO$_2$ capture in full-scale plant
Figure 7. Absorber for CO$_2$ capture

Figure 8. Spray dryer for regeneration of the liquid complex
Process Modeling

Figure 13. Contribution of major equipment to capital cost

Phase Change Ionic Material for CO$_2$ Capture

• Only some materials have $T_m^{\text{complex}} << T_m^{\text{IL}}$
• Best system operability if $T_m^{\text{IL}}$ and $\Delta H_{\text{fus}}$ large in magnitude
• Can DRAMATICALLY reduce energy load for CO$_2$ capture process
  • Partly due to phase change ($\Delta H_{\text{fus}}$)
  • Partly due to sharp increase in capacity at “phase change pressure”

- 23% parasitic power
- 4.1\$ /kWh increase in COE
- $48/\text{ton CO}_2$ avoided

Conclusions

- Ionic liquids are tunable solvents with potential for many energy related applications, including CO₂ capture
- Can make AHA ILs with 1:1 uptake and no viscosity increase upon reaction with CO₂
- Can tune ΔH_{rxt} with electron donating/withdrawing groups
- Can tune CO₂ capacity with ΔS_{rxt}
- Can take advantage of materials (PCILs) where T_{m, complex} < T_{m, unreacted}
- Phase Change Ionic Liquids just 23% parasitic energy and 4.1₵ /kWhr increase in COE
Acknowledgments

- Bill Schneider, Ed Maginn, and Mark Stadtherr and their research groups