Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Capture Technologies

Carbon Dioxide Capture from Flue Gas Using Ionic Liquids

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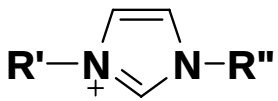
Outline

- Introduction to ionic liquids (ILs)
- ILs for capturing CO_2 from flue gas
- IL property-structure solubility relationships
- ILs for energy efficient gas separations
- Summary

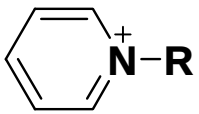
Ionic Liquids – a New Kind of Solvent

- Organic salts that are liquid at temperatures around ambient
- Liquid over a wide range of temperature; 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

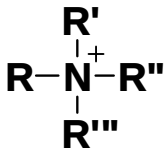
Typical Ionic Liquids



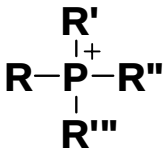
imidazolium



pyridinium



alkylammonium



alkylphosphonium

X = Cl, NO_3, CH_3CO_2, CF_3CO_2, BF_4, CF_3SO_3, PF_6, $(CF_3SO_2)_2N$

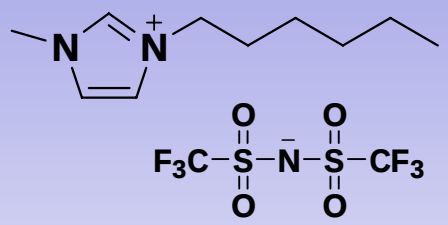
1-*n*-hexyl-3-methylimidazolium tetrafluoroborate = [hmim][BF_4]

Not all ILs created equal (viscosity, T_m, toxicity, PF_6 and BF_4 anion degradation)

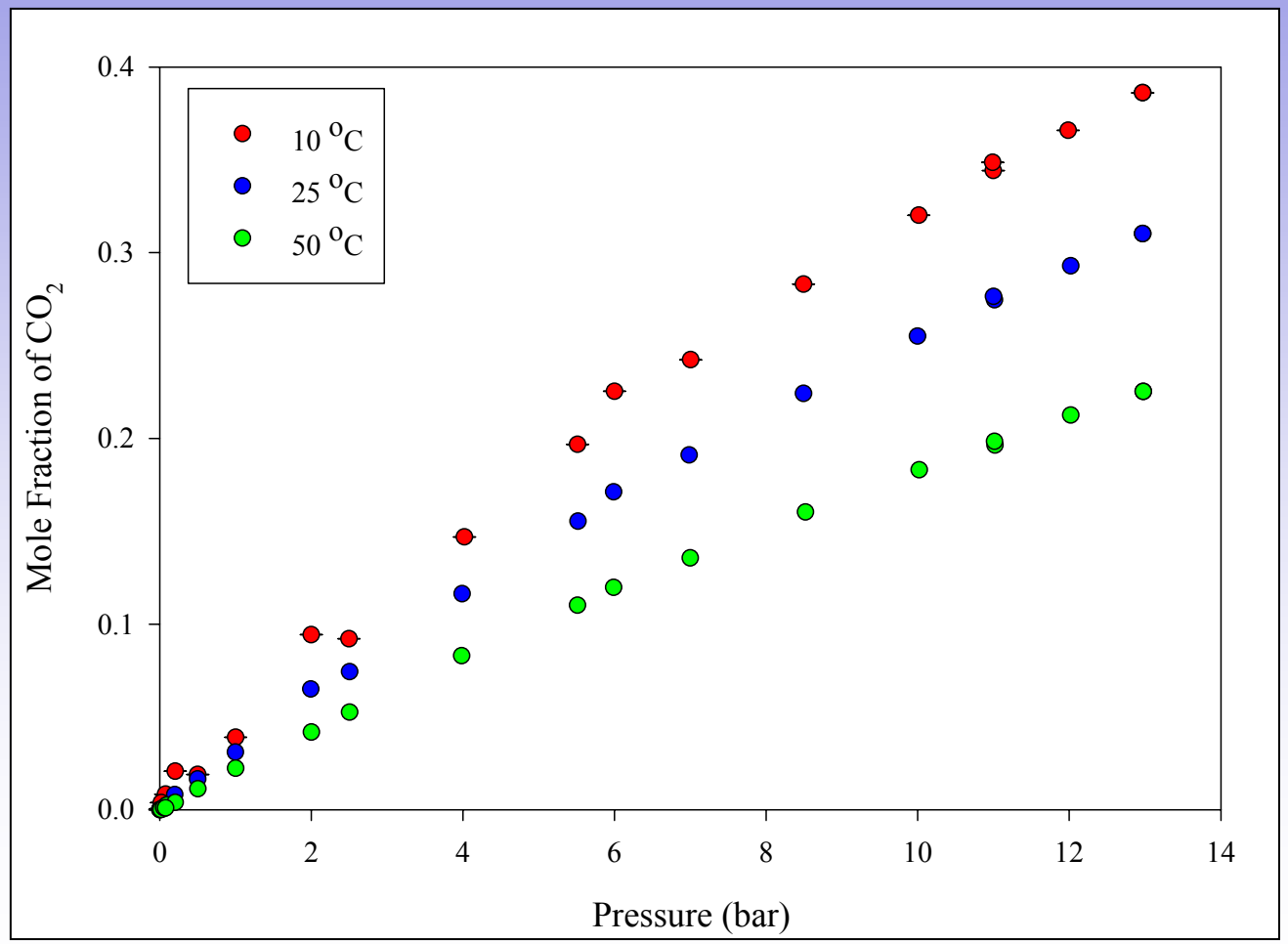
ILs for Removal of CO_2 from Flue Gas

- Idea: use ILs as absorbent to remove CO_2 from flue gas
- Solubility of CO_2, N_2, SO_2, NO_x, H_2O in ILs vitally important
- First discovered high CO_2 solubility in ILs when using SC CO_2 to extract solutes from ILs (Blanchard et al., Nature, 399, 1999, 28)
- Have measured gas solubilities in various imidazolium, quaternary ammonium, phosphonium, pyrrolidinium and pyridinium ILs

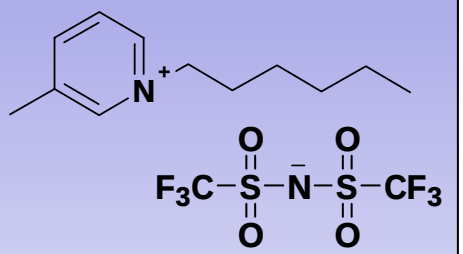
CO_2 Solubility in [hmim][Tf_2N]



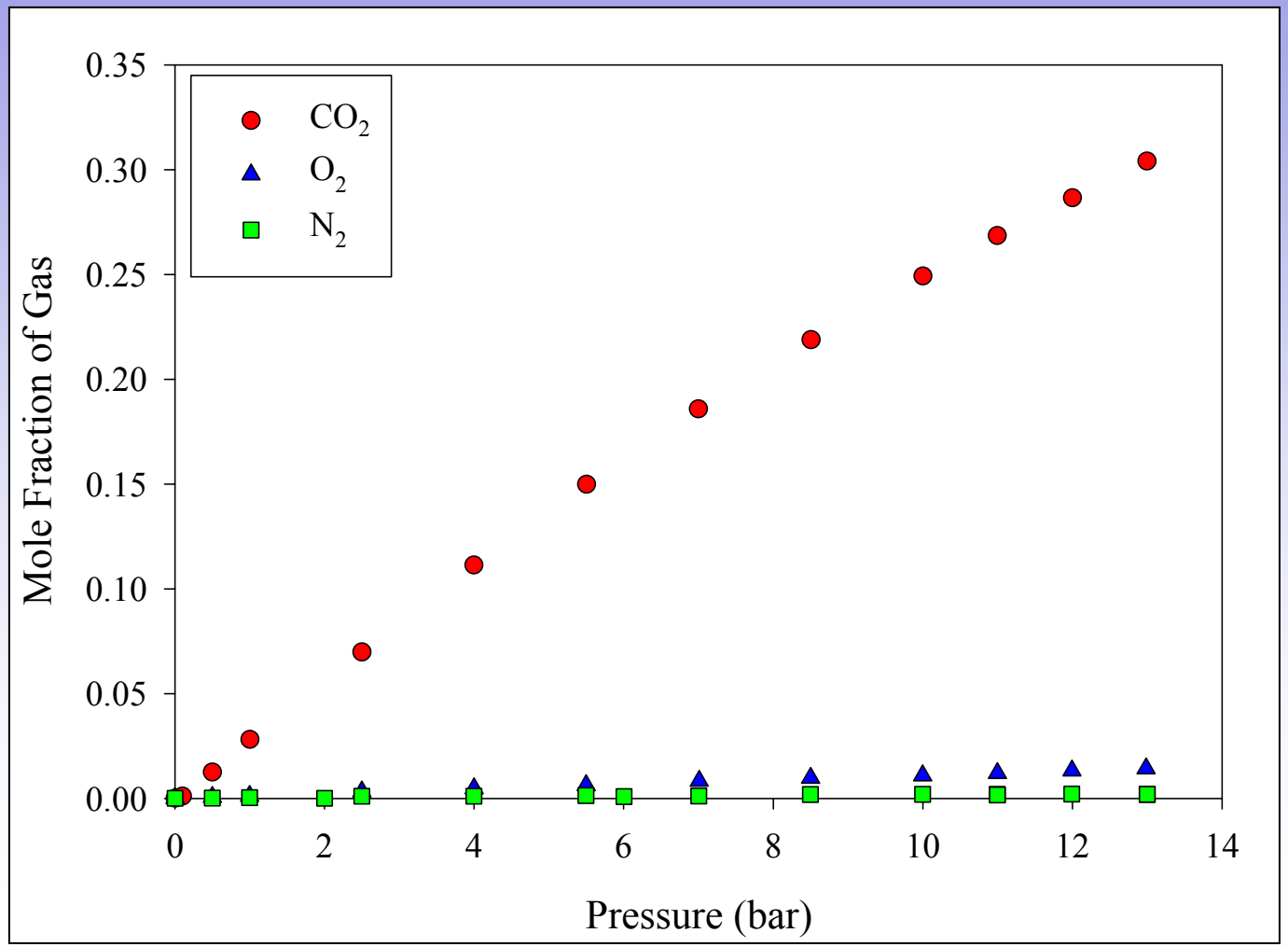
[hmim][Tf_2N]



Various Gas Solubilities in [hmpy][Tf_2N]



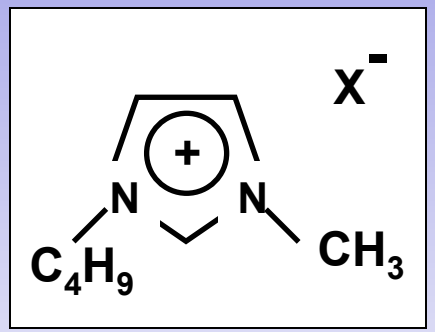
[hmpy][Tf_2N]



CO_2 (and SO_2) Solubility in "Common" ILs

- Anion effect
- Saturation with water
- Fluorinated cation
- Fluorinated anion
- Chemical absorption
- Mixture
- SO_2 vs. CO_2 solubility results
- Solubility comments

Effect of Anion



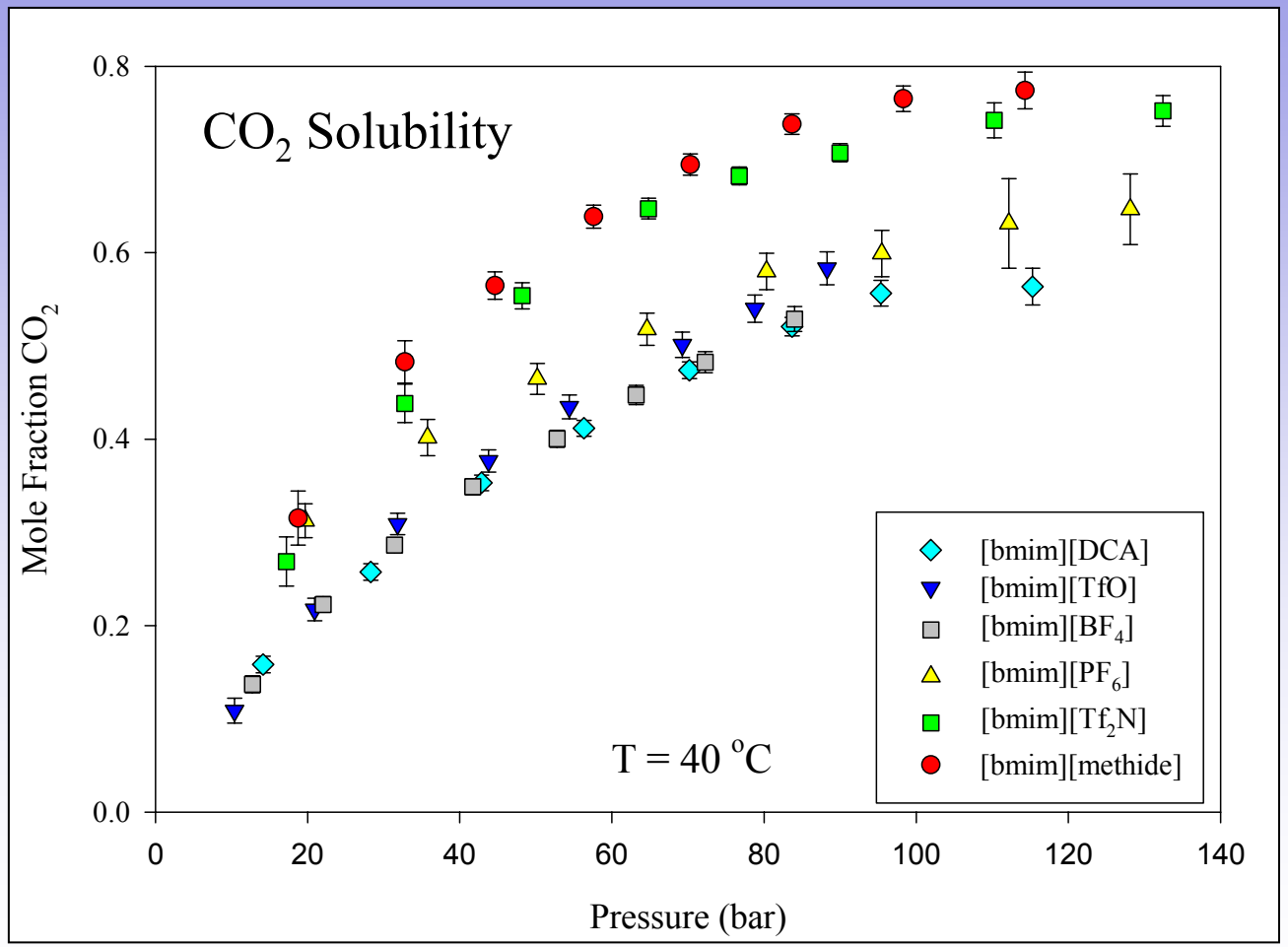
[bmim][X]

DCA = $(CN)_2N$

TfO = CF_3SO_3

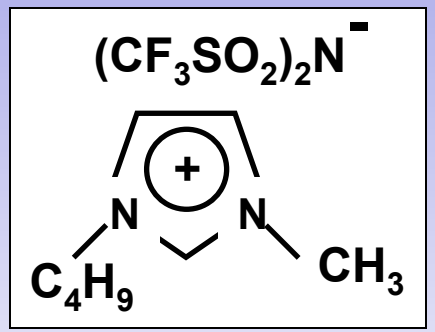
Tf_2N = $(CF_3SO_2)_2N$

Methide = $(CF_3SO_2)_3C$

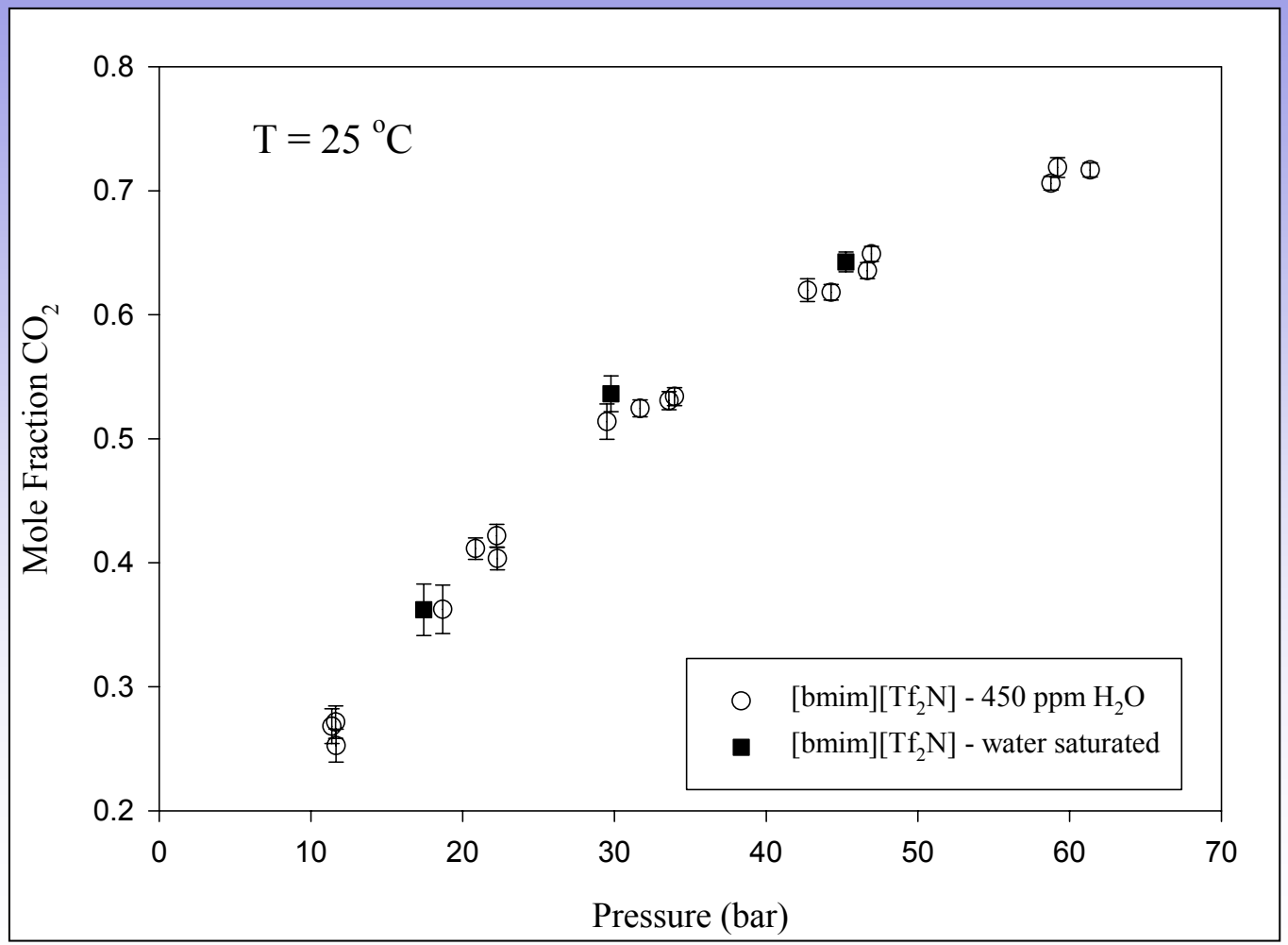


Aki et al., J. Phys. Chem. B, 108(52), 2004, 20355

Effect of Water

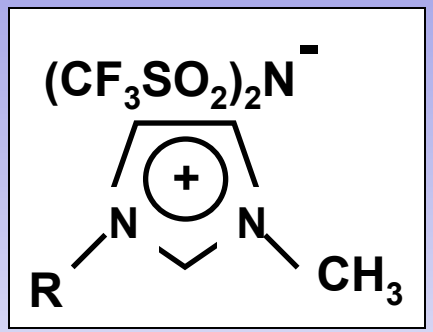


[bmim][Tf_2N]



Aki et al., J. Phys. Chem. B, 108(52), 2004, 20355

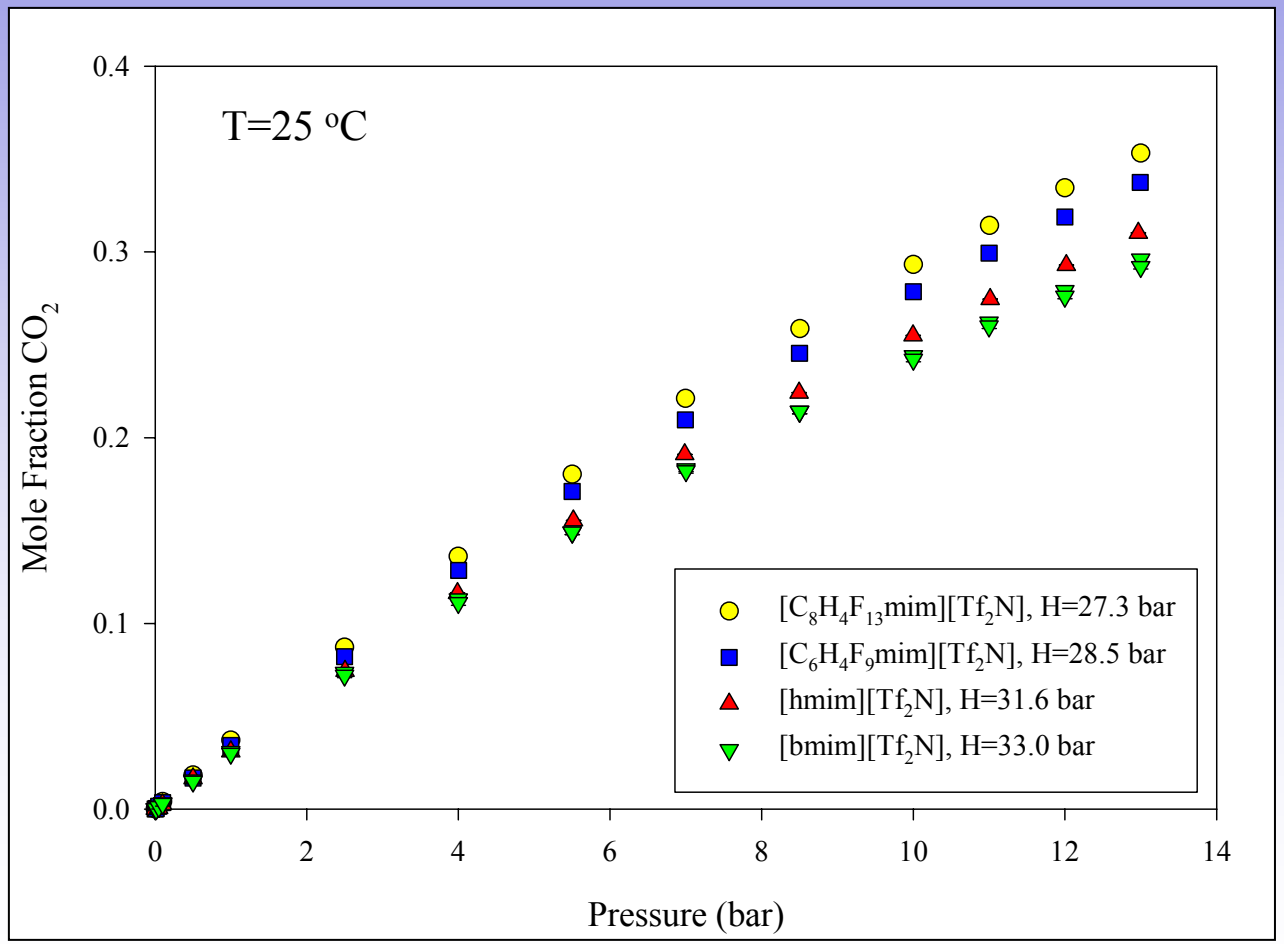
Effect of Fluorination – Cation



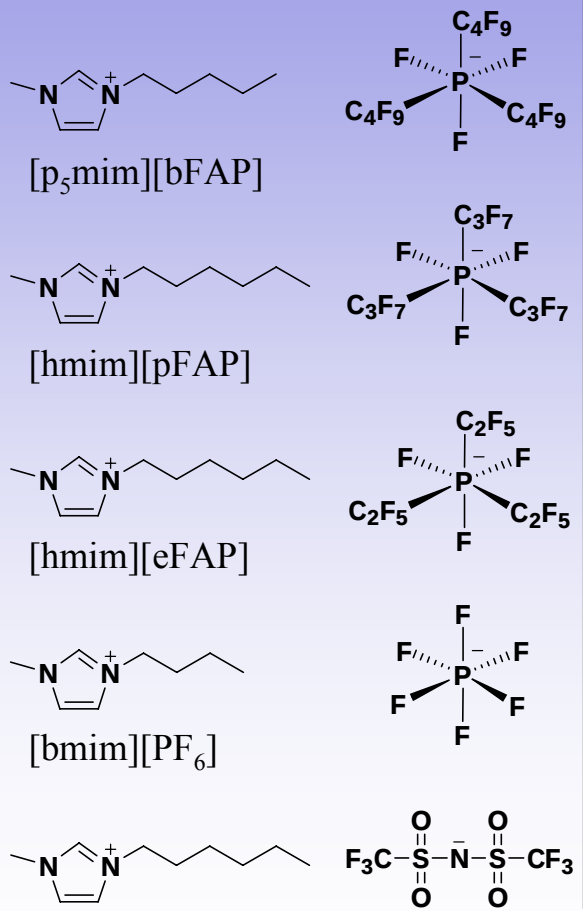
[Rmim][Tf_2N]

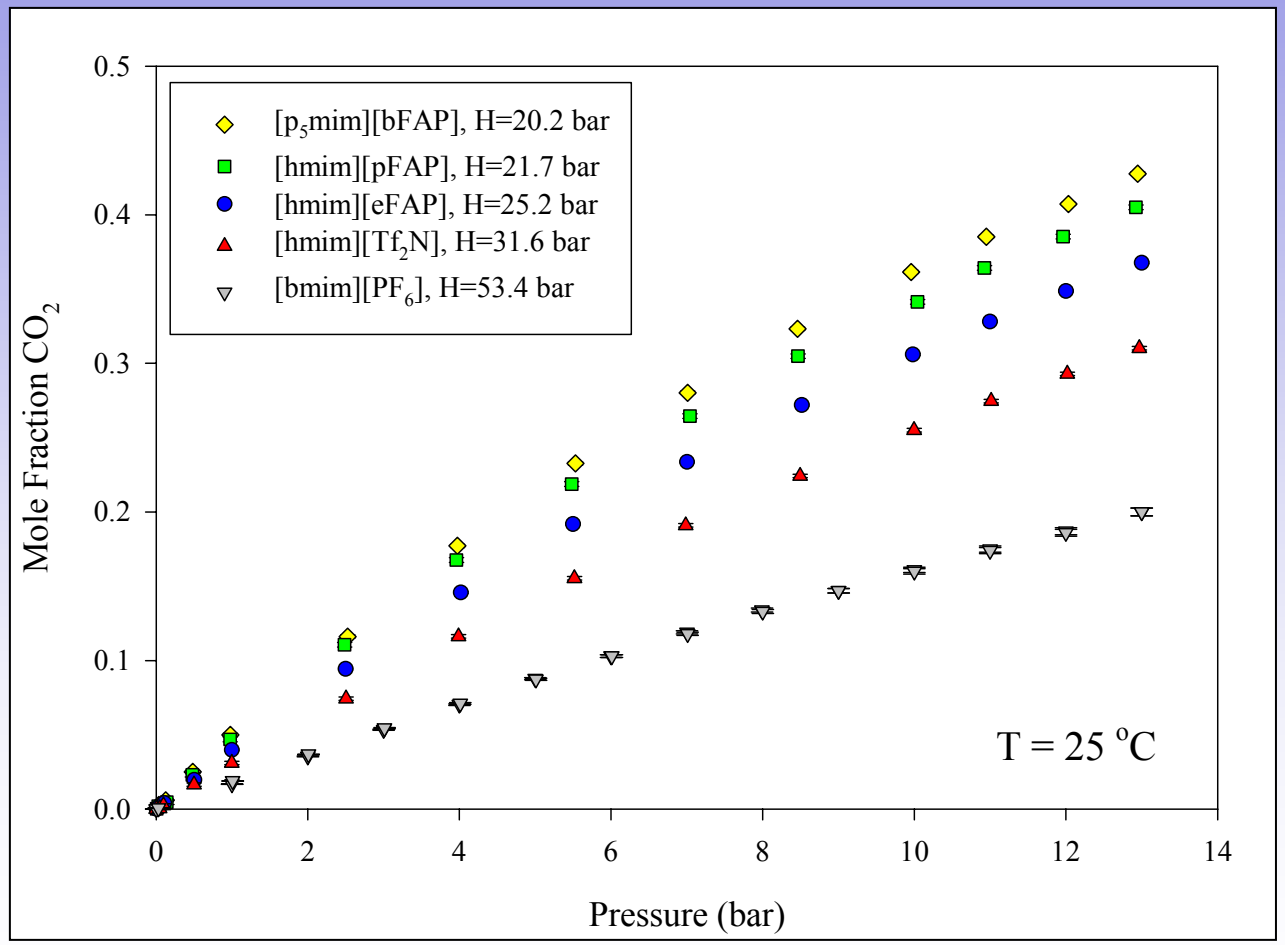
$$H \equiv \lim_{x_i \to 0} \frac{f_i^L}{x_i}$$

$$P = x\,H$$



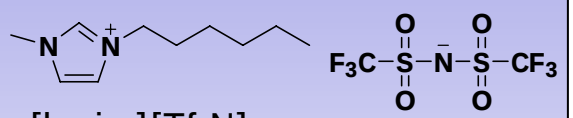
Effect of Fluorination – Anion



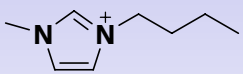


FAP samples were a gift from Merck KGaA

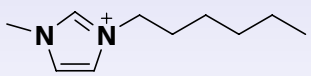
Chemical Complexation between IL and Gas



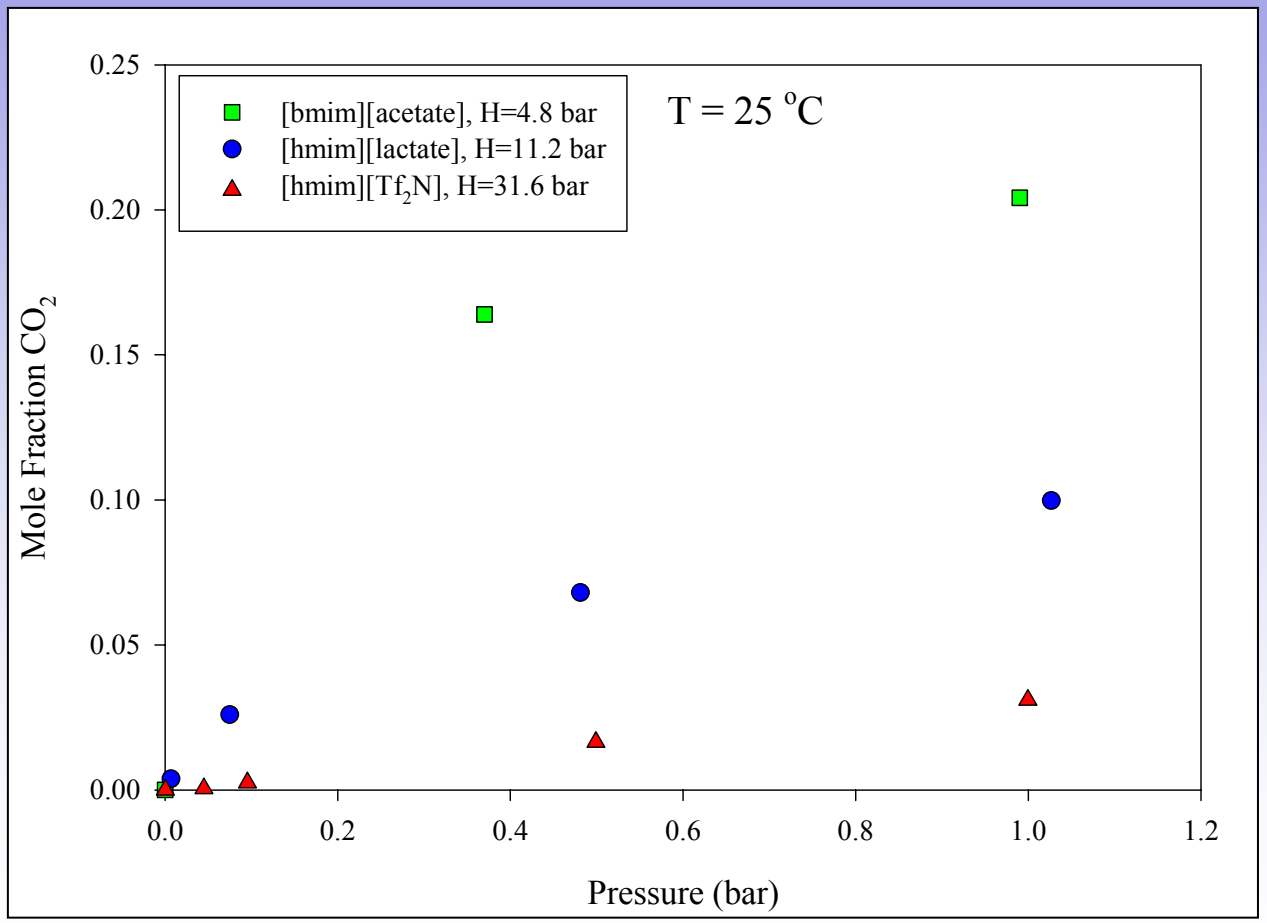
[hmim][Tf_2N]



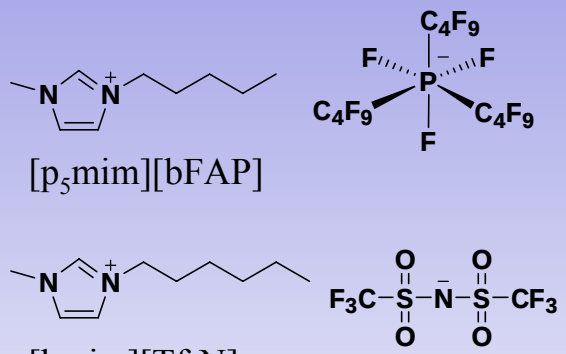
[bmim][acetate]



[hmim][lactate]

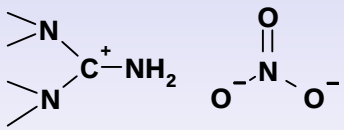


Mixture $[TMG][NO_3]+[hmim][Tf_2N]$

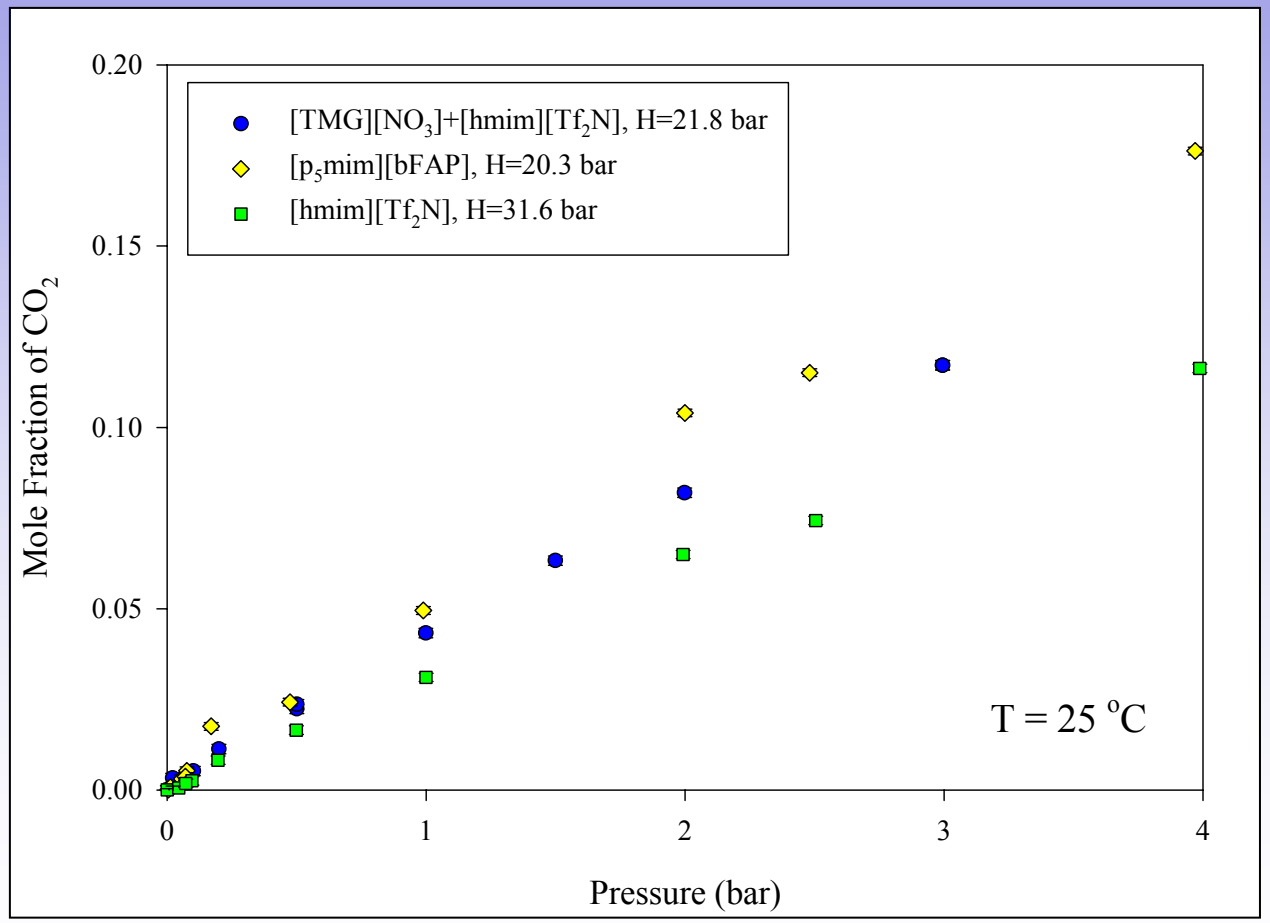


$[p_5mim][bFAP]$

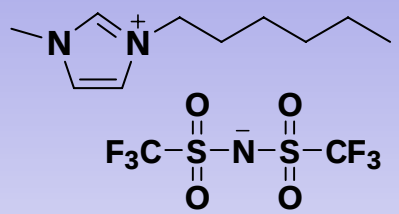
$[hmim][Tf_2N]$



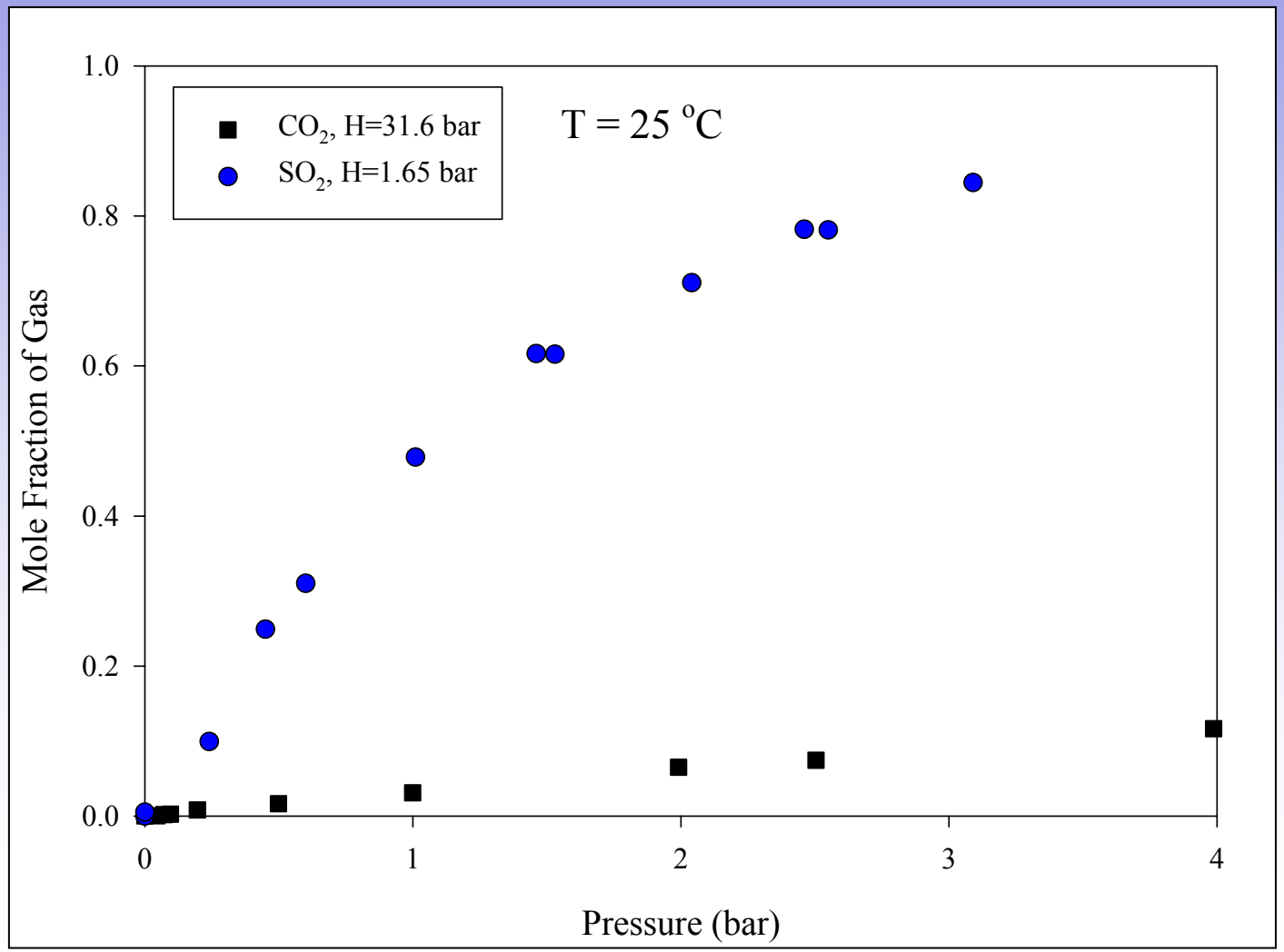
$[TMG][NO_3]$



SO_2 vs. CO_2 Solubility in [hmim][Tf_2N]

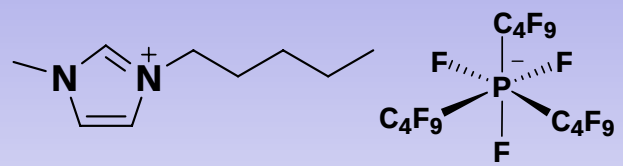


[hmim][Tf_2N]



Solubility Comments

- Compound with best CO_2 solubility from physical absorption has H=20.2 bar at 25ºC



- Potentially H~15 bar for fluorinated anion AND cation
- Higher carrying capacity for chemical complexation; e.g., [bmim][acetate], H=4.8 bar
- Tf_2N ILs water immiscible
- TMG ILs very promising
- ILs will remove SO_2, as well, in single step

Systems Analysis

- Preliminary systems/economic analysis underway (Trimeric Corporation)
- Objectives
  - Evaluate economic feasibility
  - Determine targets for IL properties to meet DOE CO_2 capture cost goals
- Method
  - Use IL/CO_2 test data
  - Estimate capital and operating costs
  - Overall systems economics using NETL guidelines
  - Determine sensitivity to key process variables

Results Comments

- Conventional absorber/stripper configuration
- Supported liquid membrane
  - Use small amount of IL
  - Solution/diffusion mechanism
  - Good long term stability; no evaporation
- [hmim][Tf_2N] being tested in supported liquid membrane configuration at NETL for flue gas cleanup
- Better application may be removal of CO_2 from syngas in IGCC power generation
  - High pressure

Summary

- Ionic liquids are tunable solvents with wide variety of potential applications
- Gas solubilities vary significantly
- Fluorination increases CO_2 solubility
- Higher carrying capacity obtained through chemical complexation
- Simultaneous removal of CO_2 and SO_2
- ILs currently being tested for flue gas cleanup in supported liquid membrane contactor
- Potential for other energy efficient gas separations

Acknowledgements

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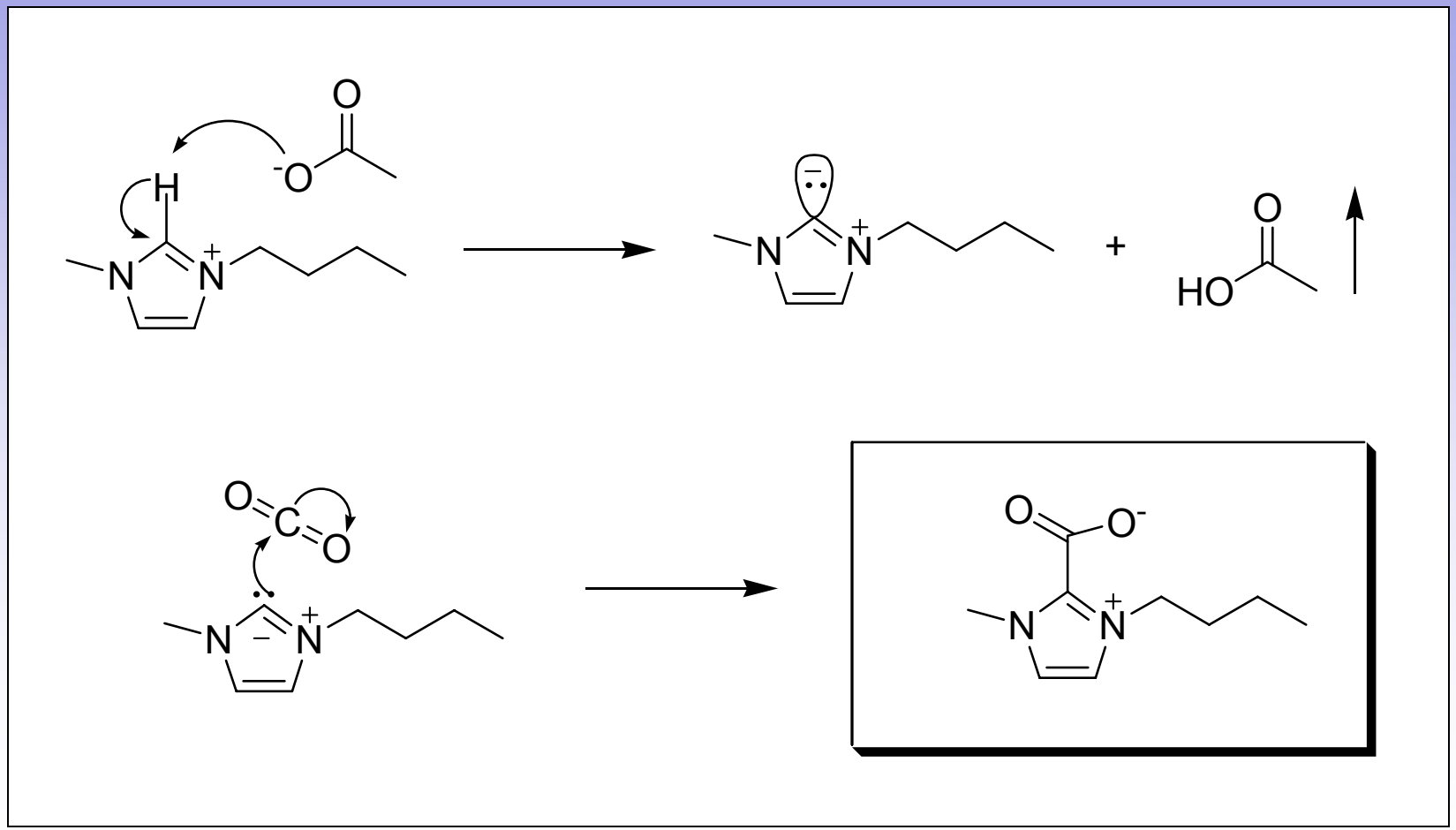
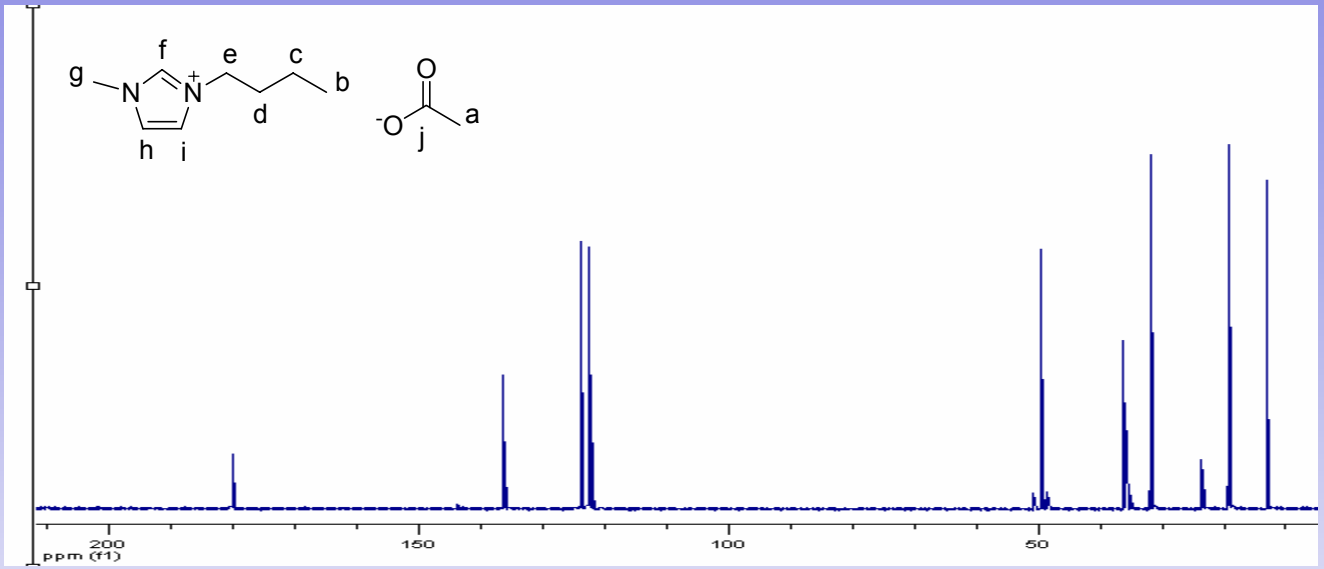
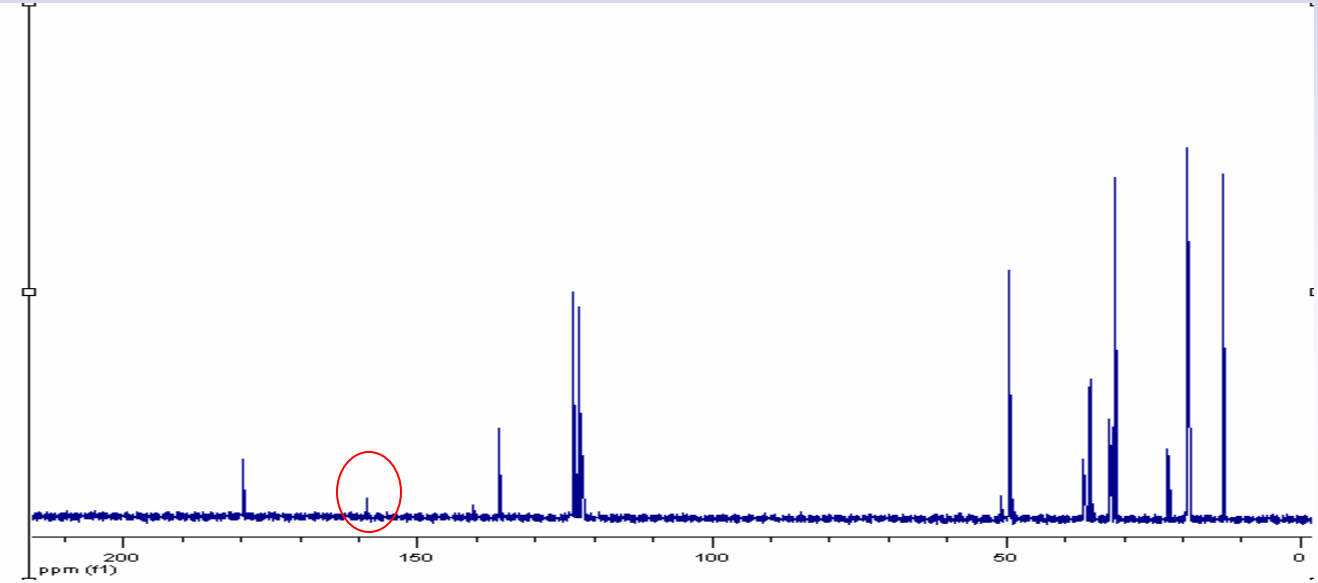
- US Department of Education - GAANN
- State of Indiana 21st Century Research and Technology Fund
- Reilly Industries

Solubility Mechanism for Chemical Complexation



^{13}C NMR of [bmim][acetate]