Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Capture - Membranes

Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents for Sequestration

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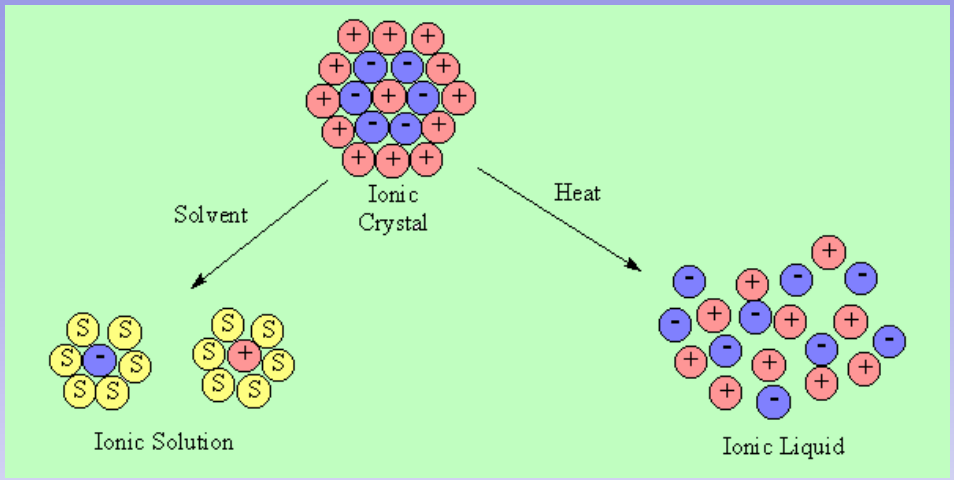
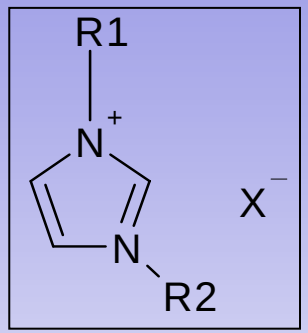
What are ionic liquids?



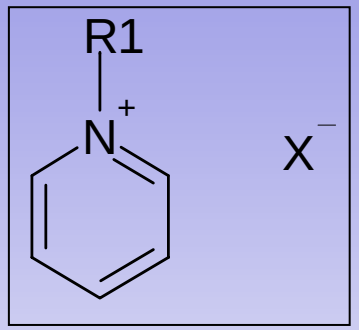
- They are *not* ionic solutions
- They are *not* ionic crystals
- They *are* molten salts that happen to be “molten” around ambient temperature

Typical compounds

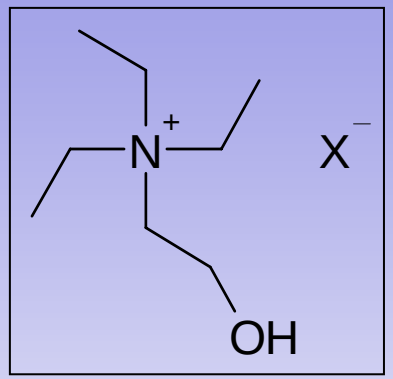
Examples of some possible cations and anions



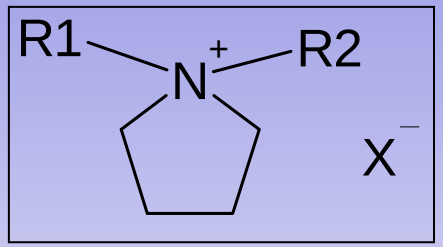
dialkylimidazolium



alkylpyridinium



trialkylethoxy



pyrrolidinium

X$^-$ =

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

Example of naming convention:
1-n-butyl-3-methylimidazolium tetrafluoroborate = [bmim][BF_4]

Many others – 10^6 or more possible permutations!

Properties of Typical ILs

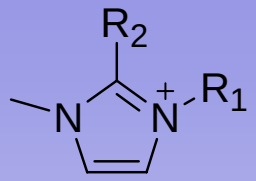
- No measurable vapor pressure (“green”?)
- Non-flammable
- Liquid over wide range (-90 ^{o}C to > 200 ^{o}C)
- Highly solvating – low volumes required
  - Organic, inorganic, polymeric materials
- Can be catalytic as well as a solvent
- Many potential applications
  - Separations
  - Lubricants
  - Heat transfer / thermal fluids
  - Plasticizers

J. F. Brennecke and E. J. Maginn, “Ionic Liquids: Innovative Fluids for Chemical Processing" *AIChE Journal* **2001**, 47, 2384-2389

Goal of NETL-sponsored project

- Evaluate feasibility of using ionic liquids for CO_2 capture
  - Technical feasibility
    - CO_2 selectivity, capacity
    - Stability
    - Cost
  - Can we “design” better ionic liquids?
    - Synthesize and test new molecules
    - Use molecular modeling to gain fundamental understanding
  - Method of use
    - Liquid absorbent
    - Supported liquid membrane
    - Physical / chemical absorbent

Cations

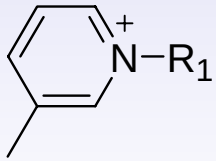


[bmim]: $R_1 = C_4H_9$, $R_2 = H$

[hmim]: $R_1 = C_6H_{13}$, $R_2 = H$

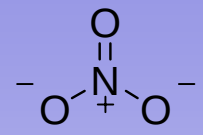
[hmmim]: $R_1 = C_6H_{13}$, $R_2 = CH_3$

[omim]: $R_1 = C_8H_{17}$, $R_2 = H$

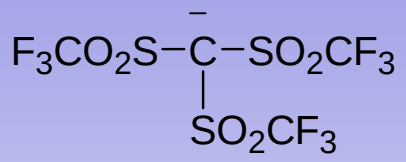


[hmpy]: $R_1 = C_6H_{13}$

Anions

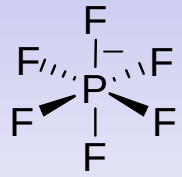


$[NO_3]$

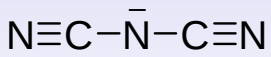


[methide]

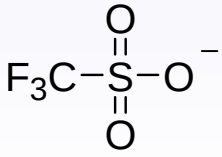
$[BF_4]$



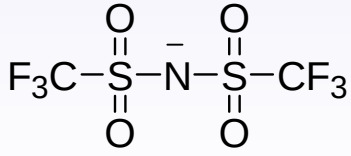
$[PF_6]$



[DCA]

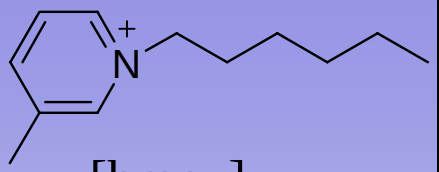


[TFO]

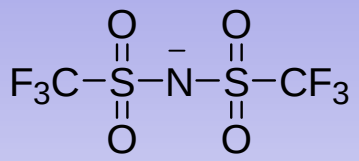


$[TF_2N]$

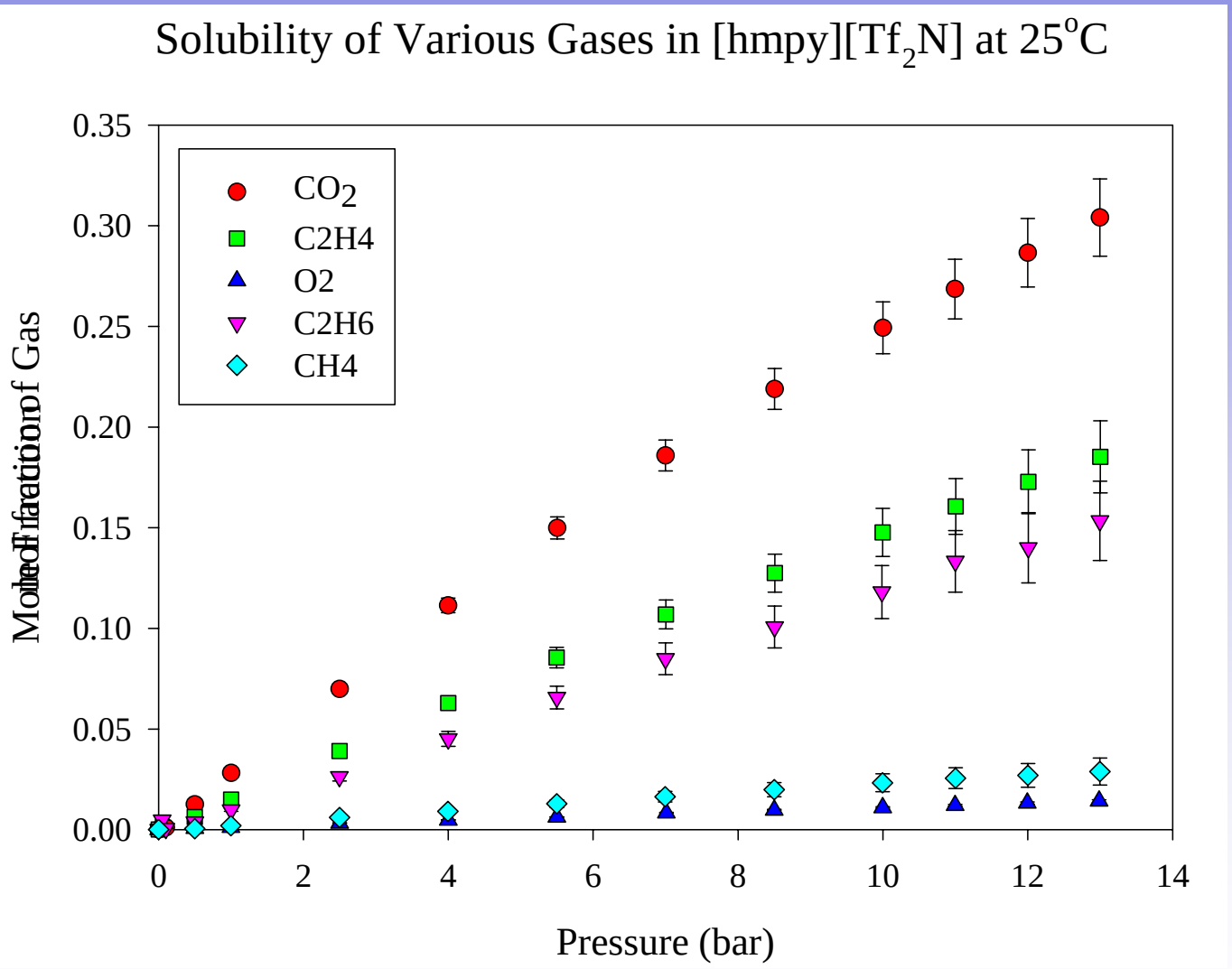
Previous Results



[hmpy]

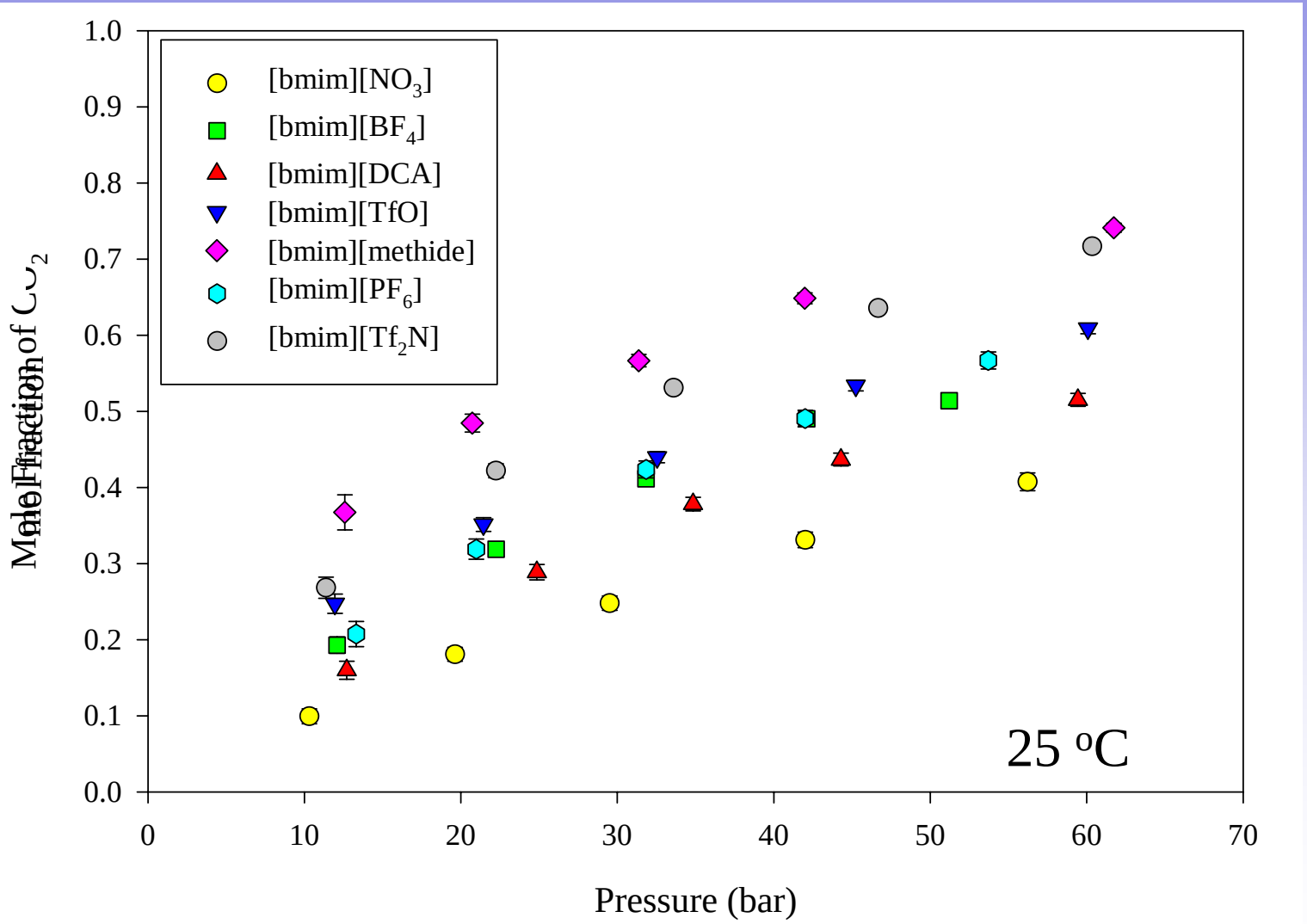


[TF_2N]

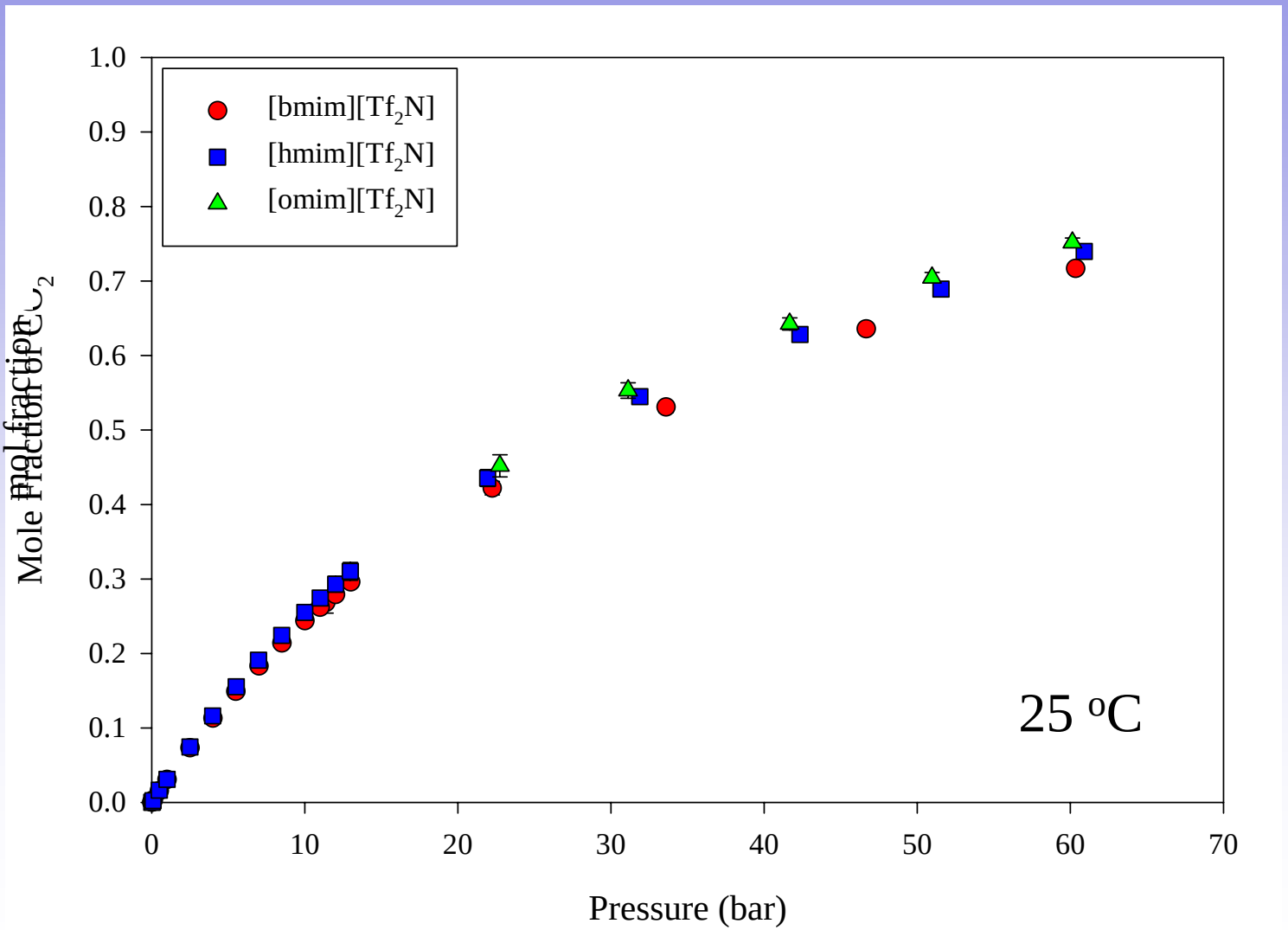


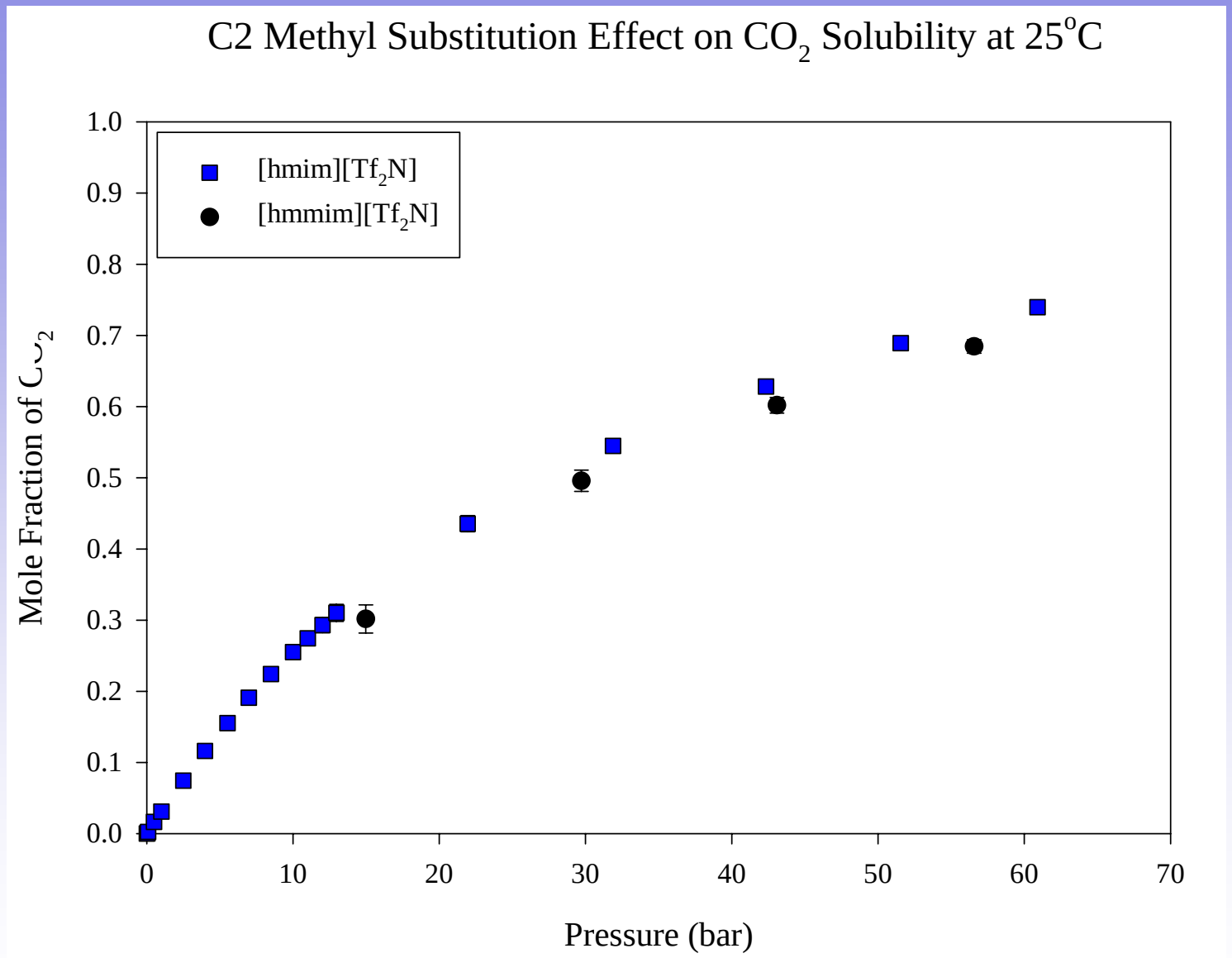
Large CO_2 capacity, good selectivity for physical absorbent!

Anion Has Large Effect on CO_2 Solubility



Cation Has Smaller Effect on CO_2 Solubility



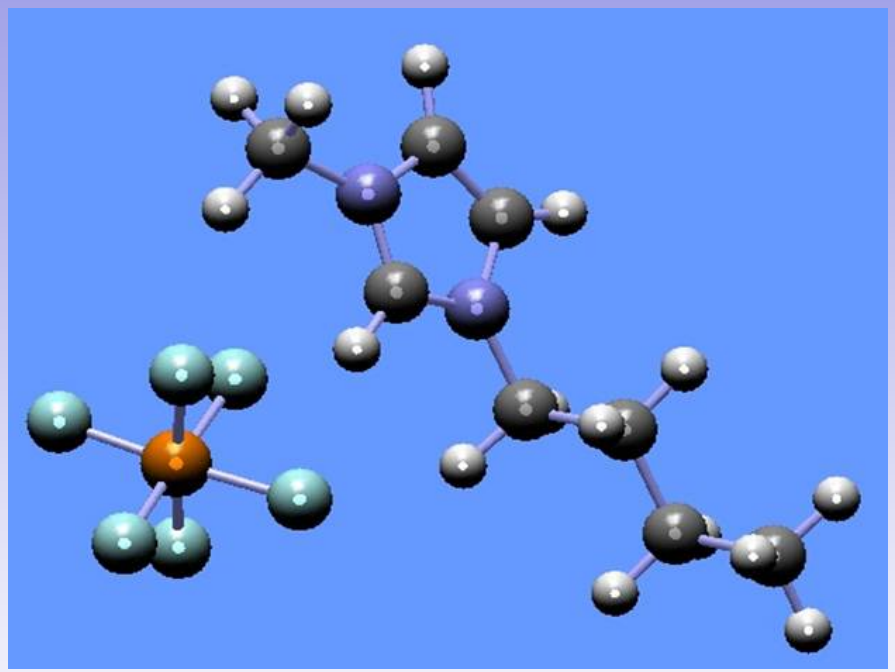

C2 Methyl Substitution Effect on CO_2 Solubility at 25°C
[hmim][Tf2N]
[hmmim][Tf2N]
Mole Fraction of CO2
Pressure (bar)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
10
20
30
40
50
60
70

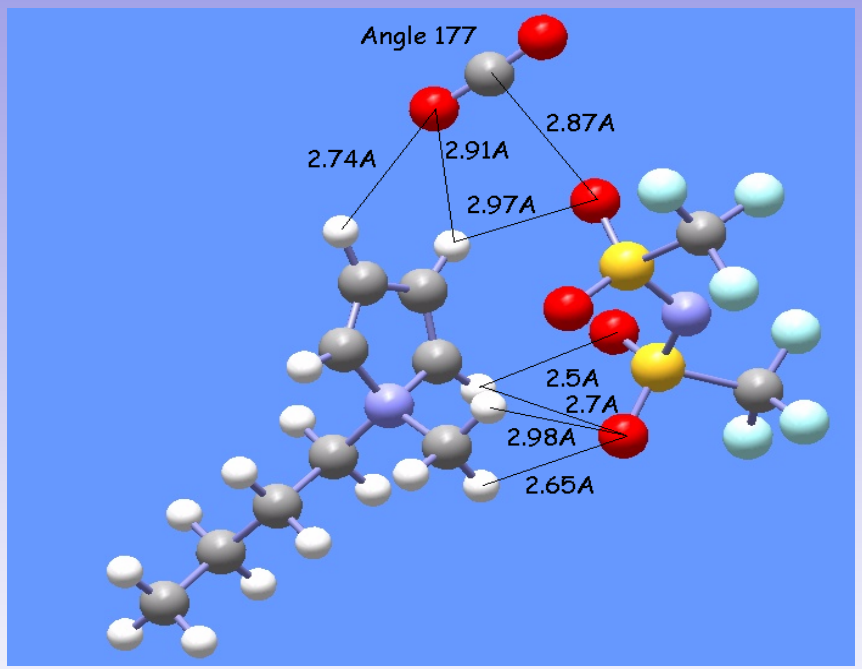
Results from Current Project: Physical Absorbents

- Molecular modeling to understand CO_2 solubility
- Synthesis of new compounds
- Experimental solubility measurements

Molecular Modeling

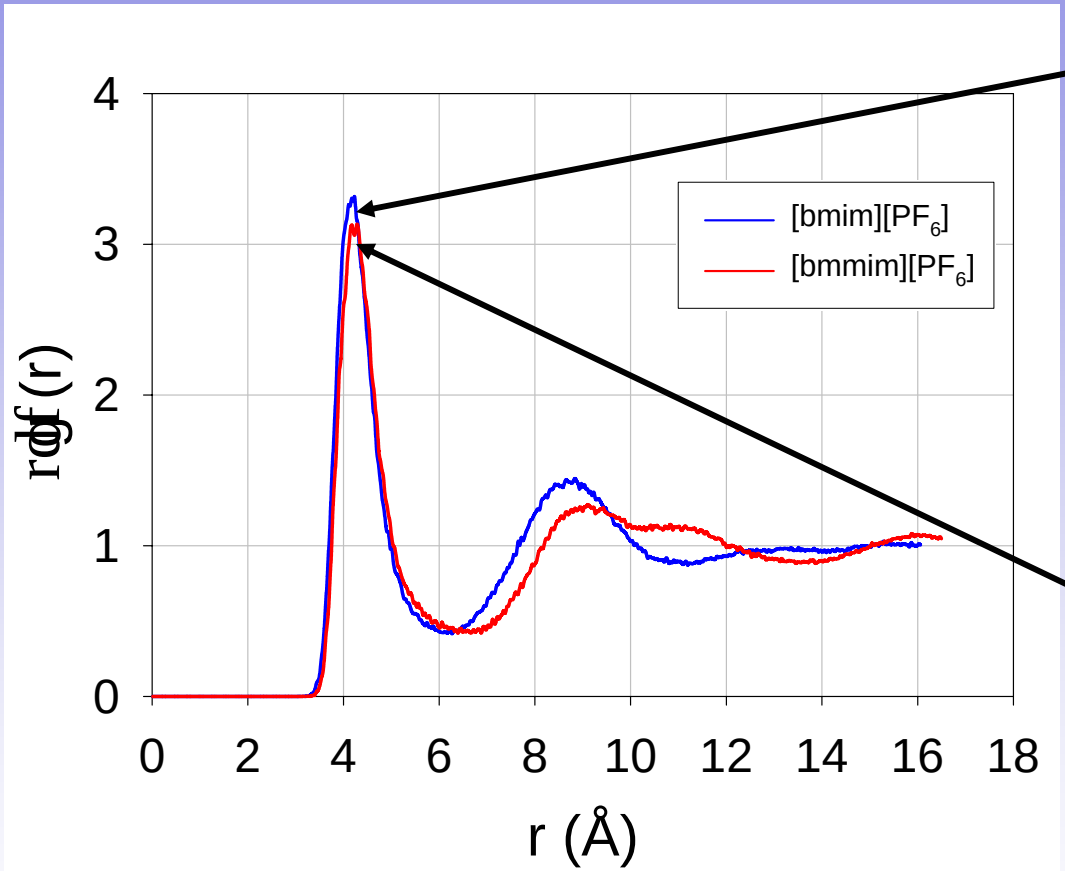
Gas phase *ab initio* calculations (B3LYP/6-311+G*)

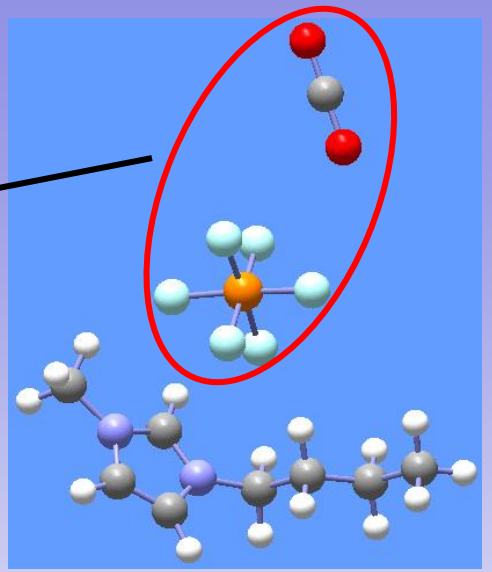


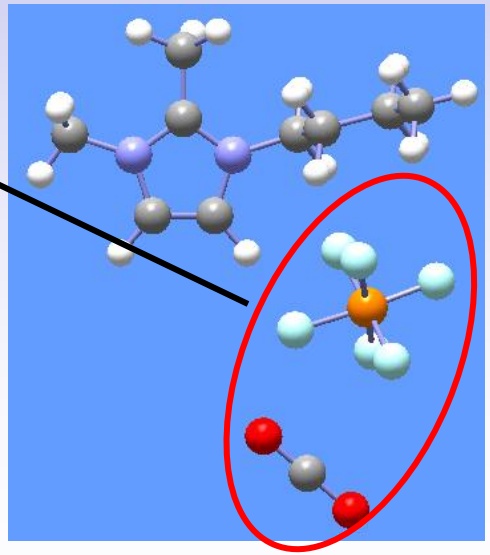


- Structure of single ion pairs
- Local ordering and energetics of CO_2 binding
- Potential parameters for classical condensed phase simulations

Condensed Phase Simulations

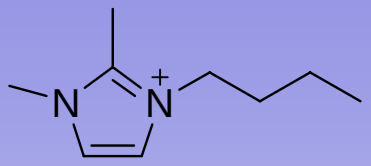




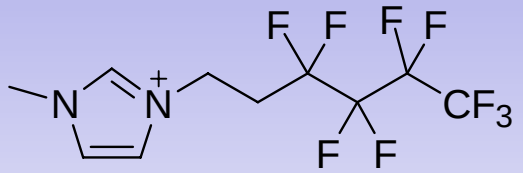


Strong CO_2 association with anion, regardless of the cation: *anion dominates CO_2 physical absorption behavior*

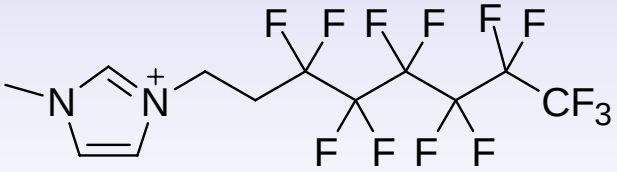
New Cations



[bmmim]

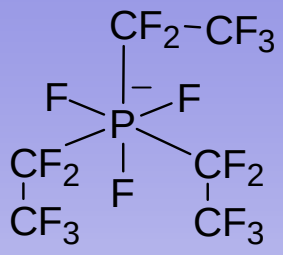


[$C_6H_4F_9mim$]

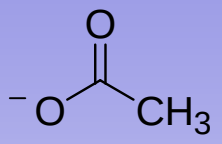


[$C_8H_4F_{13}mim$]

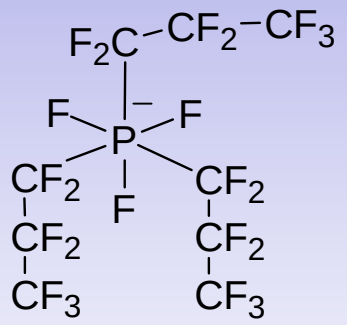
New Anions



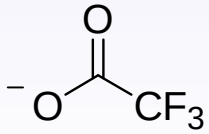
[eFAP]



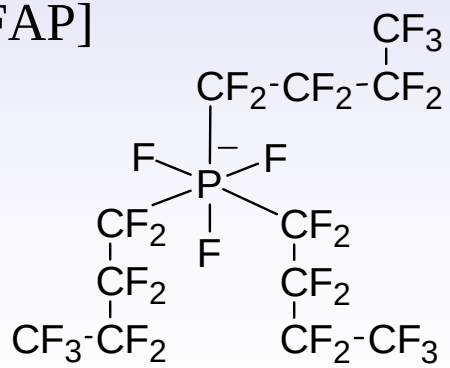
[acetate]



[pFAP]

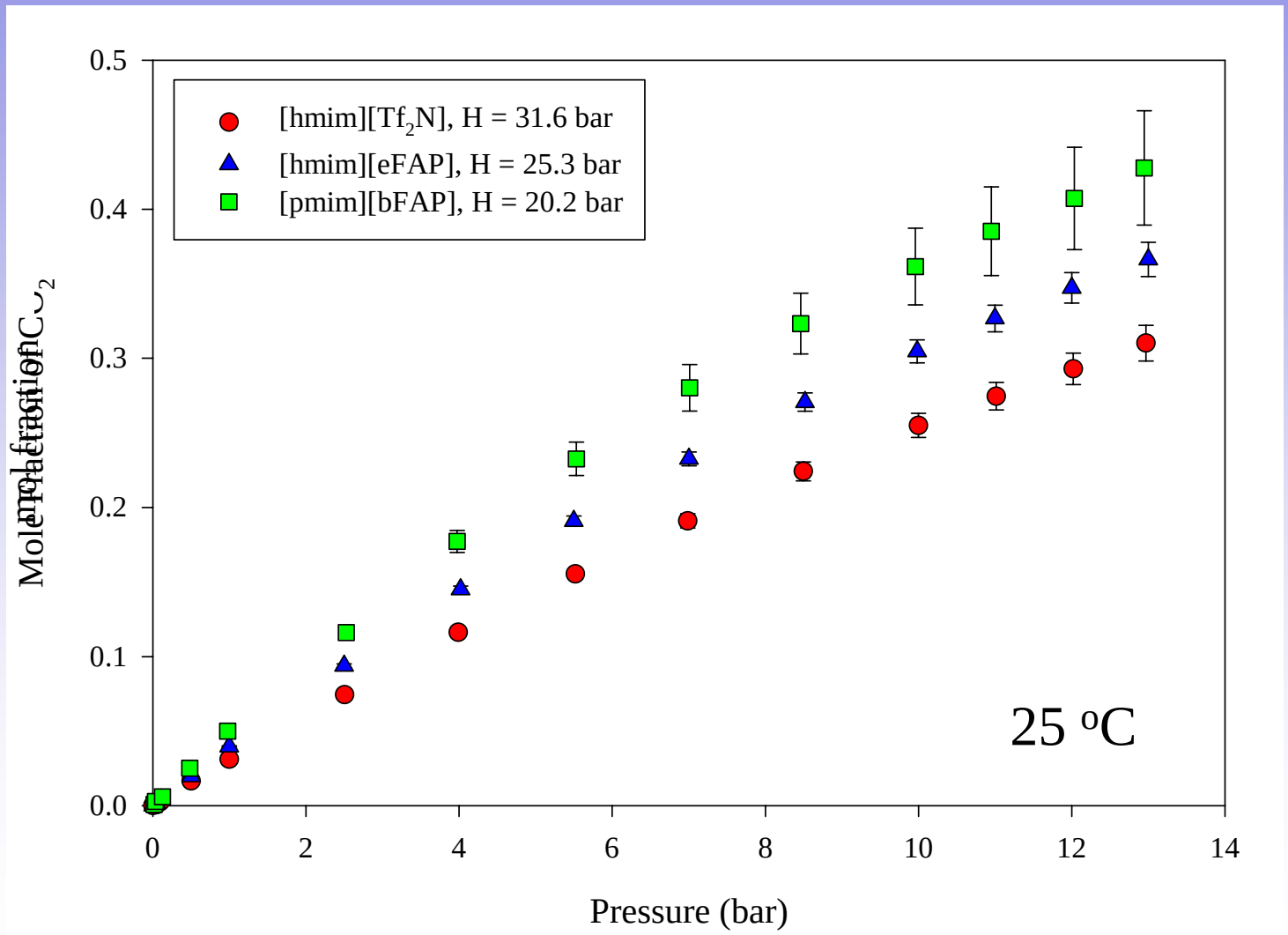


[TFA]

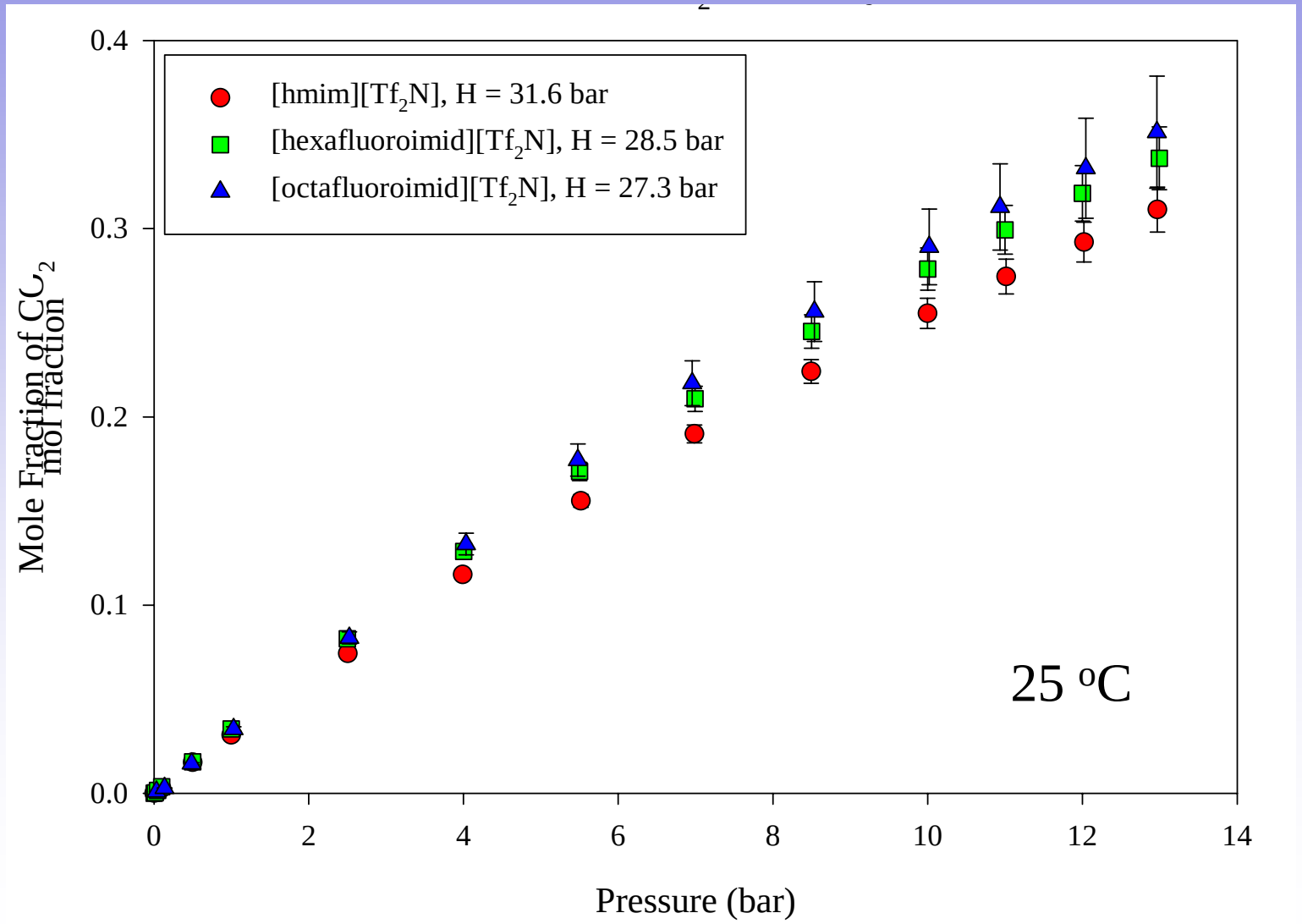


[bFAP]

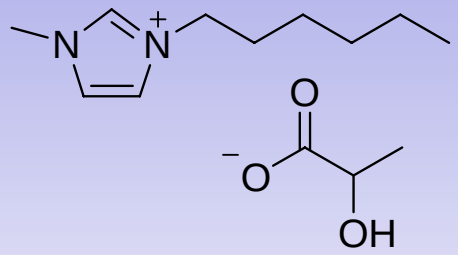
Anion Fluorination Increases CO_2 Solubility



Cation fluorination has small effect

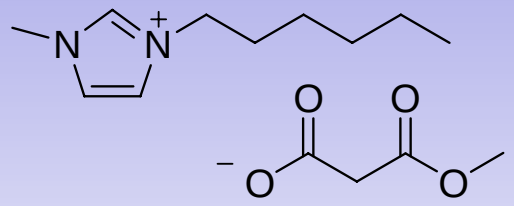


Synthesized, but not yet tested



1-hexyl-3-methylimidazolium lactate

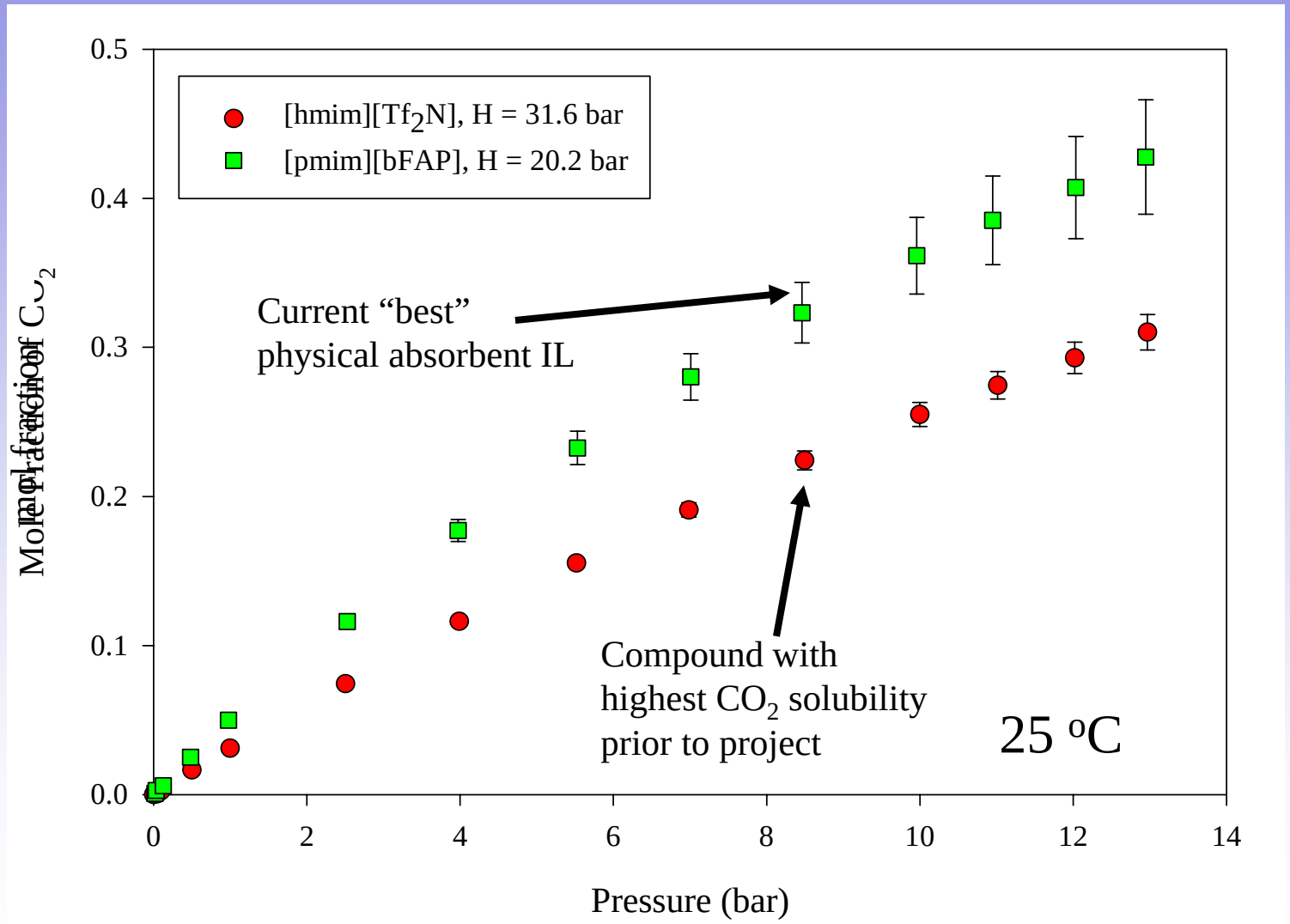
[hmim][lactate]



1-hexyl-3-methylimidazolium methylmalonate

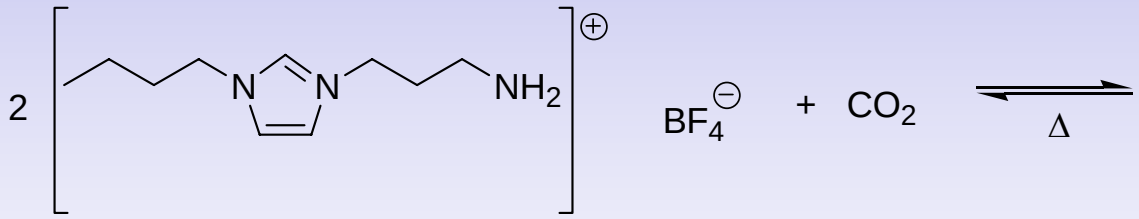
[hmim][mm]

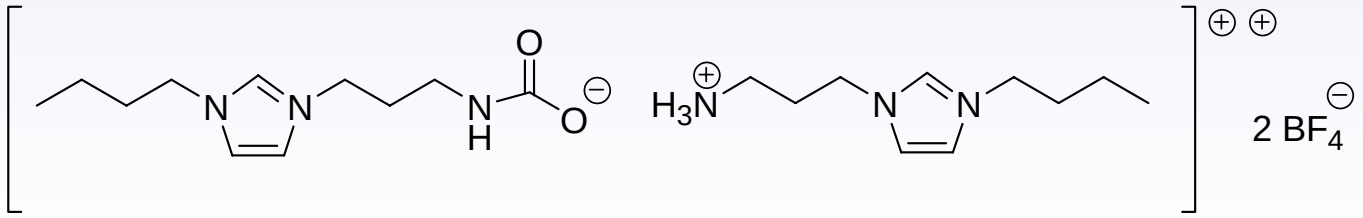
Results so far: 56% improvement in CO_2 Solubility



Chemical vs. Physical Absorption

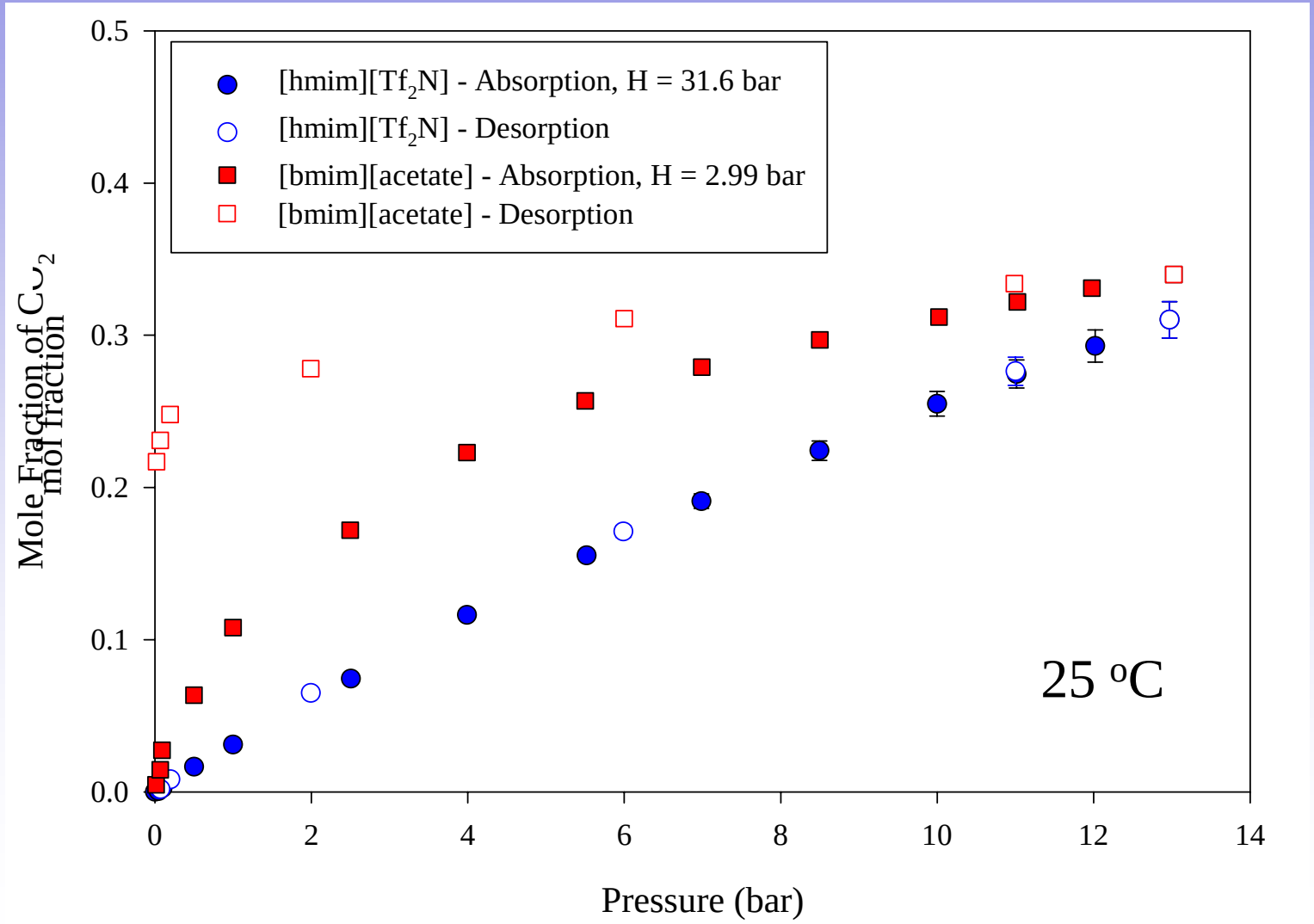
- Chemical complexation: functionalize ionic liquid to mimic amine
  - Stronger absorption…
  - but higher energy cost for regeneration



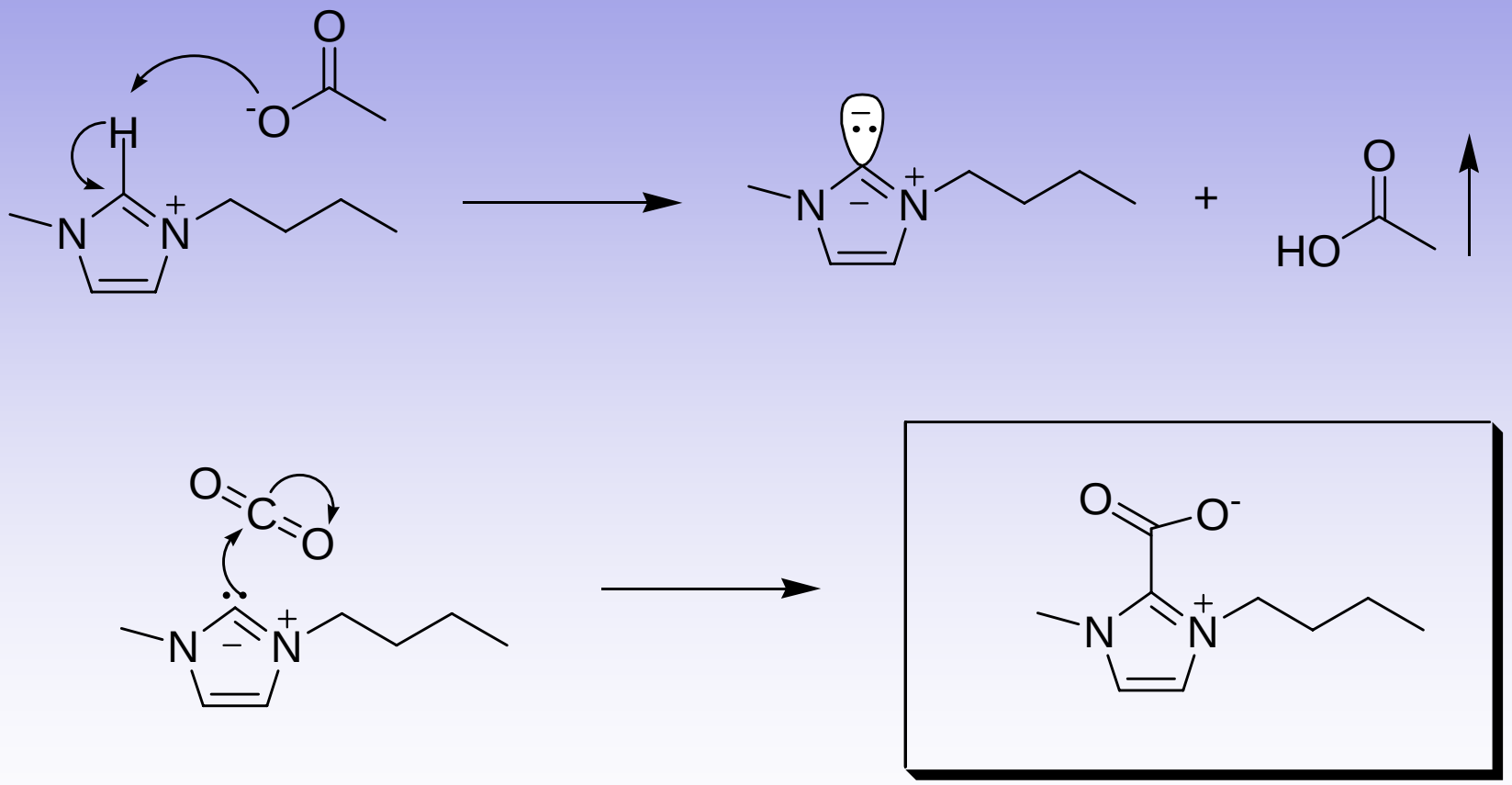


Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, H. D., *J. Am. Chem.*, **2002**, *124*, 926.

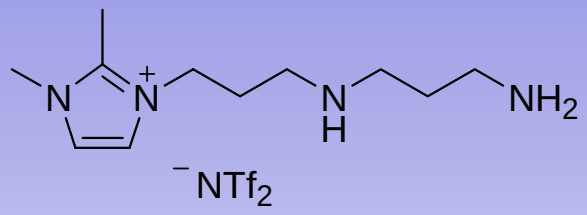
Evidence for chemical complexation with acetate anion



Proposed Mechanism for CO_2 with [bmim][acetate]



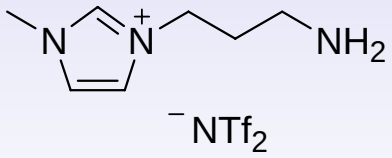
“Task-Specific” Ionic Liquids



Good yields

Good purity

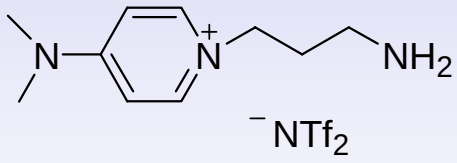
Reasonable stability



Low yields

Moderate purity

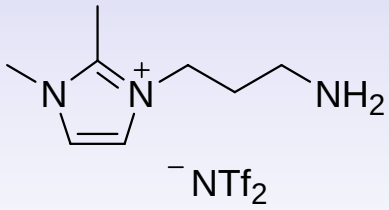
Quickly degrades



Good yields of Br

Poor purity

Water soluble



Improving yields

Improving purity

Reasonable stability

Summary

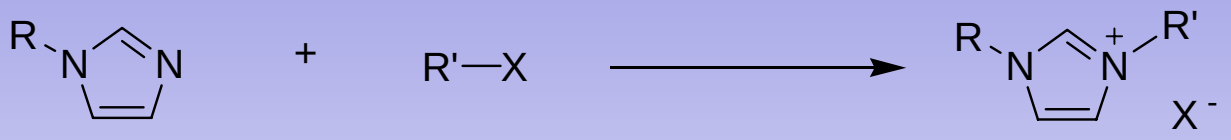
- Initiated feasibility study of using ionic liquids for CO_2 capture
  - Physical
  - Chemical
- Gaining an understanding of the factors responsible for high capacity / solubility
- Synthesized several new ionic liquid compounds
- Demonstrated 56% increase in low pressure CO_2 physical sorption over previous liquids
  - Expect to do even better
- Investigating new compounds
  - Chemical complexation
  - Better physical absorption

Acknowledgements

- Funding:
  - US Department of Energy, National Energy Technology Laboratory (DE-FG26-04NT42122)
- Research Team
  - Prof. Joan Brennecke
  - Dr. JaNeille Dixon
  - Jessica Anderson
  - Dr. Haizhong Zhang
  - Dr. Sudhir Aki
  - Dr. Mark Muldoon

General Synthesis

Step 1:



R = CH_3

R' = C_4H_9, C_6H_{13}

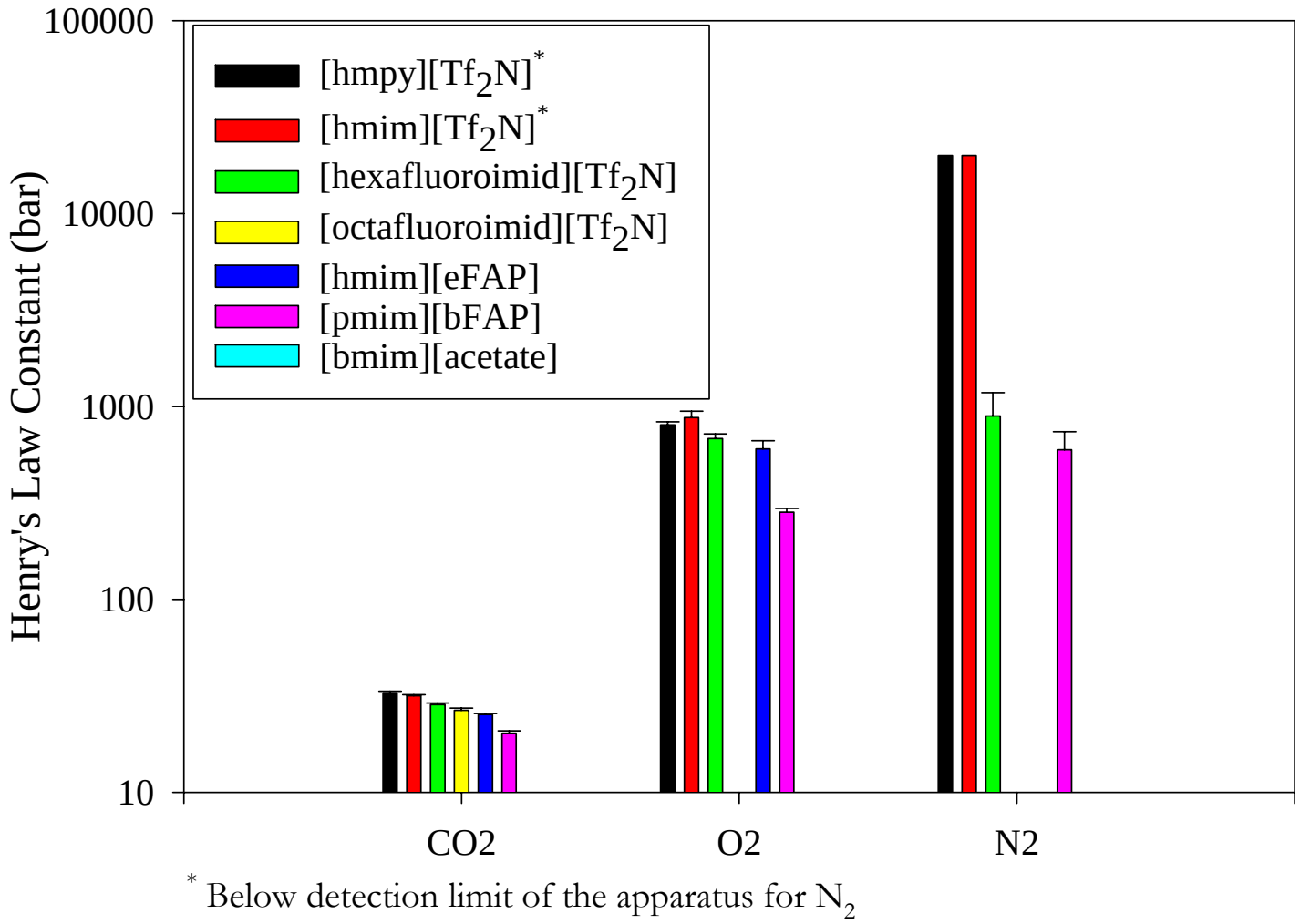
X = Cl^-, Br^-

Step 2:

M = Li, Na, K, Ag

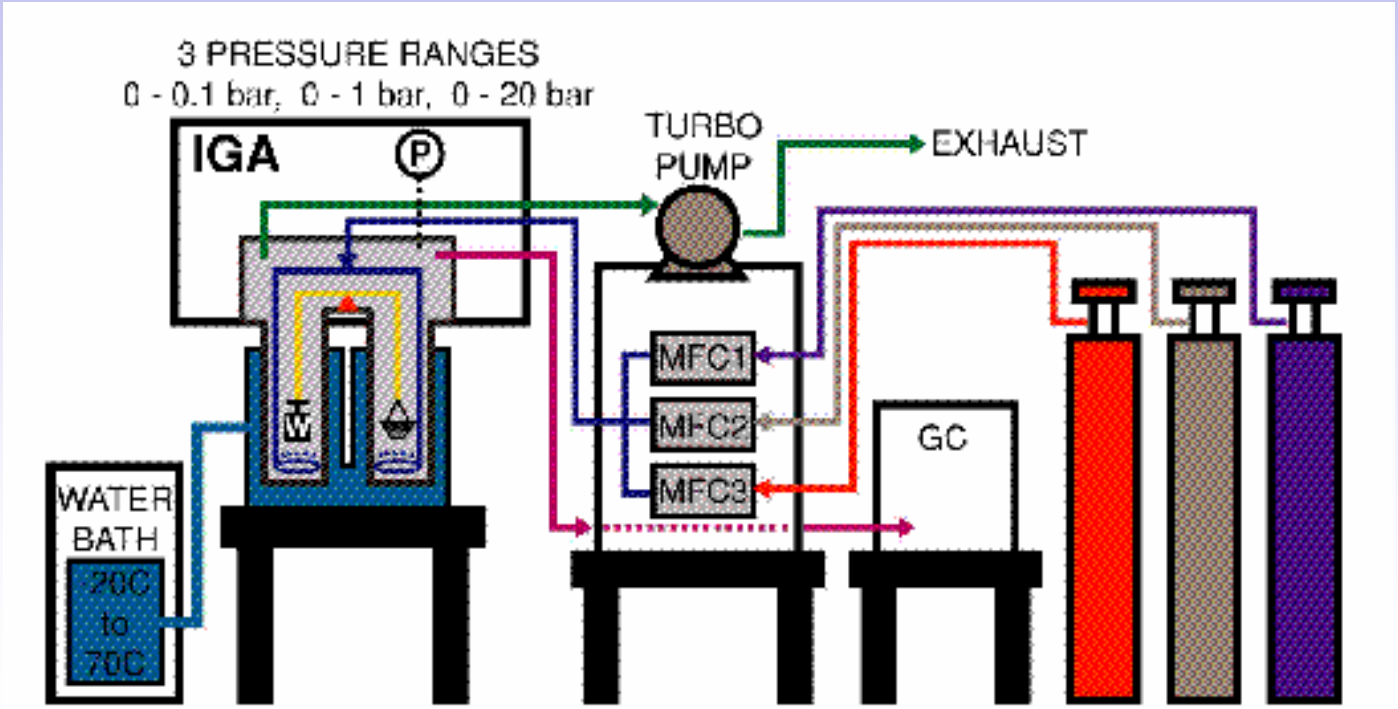
Y = PF_6, BF_4, NO_3,
CF_3SO_3, $(CF_3SO_2)_2N$

Henry's Law Constants for CO_2, O_2, and N_2 in Several ILs at 25°C



* Below detection limit of the apparatus for N_2

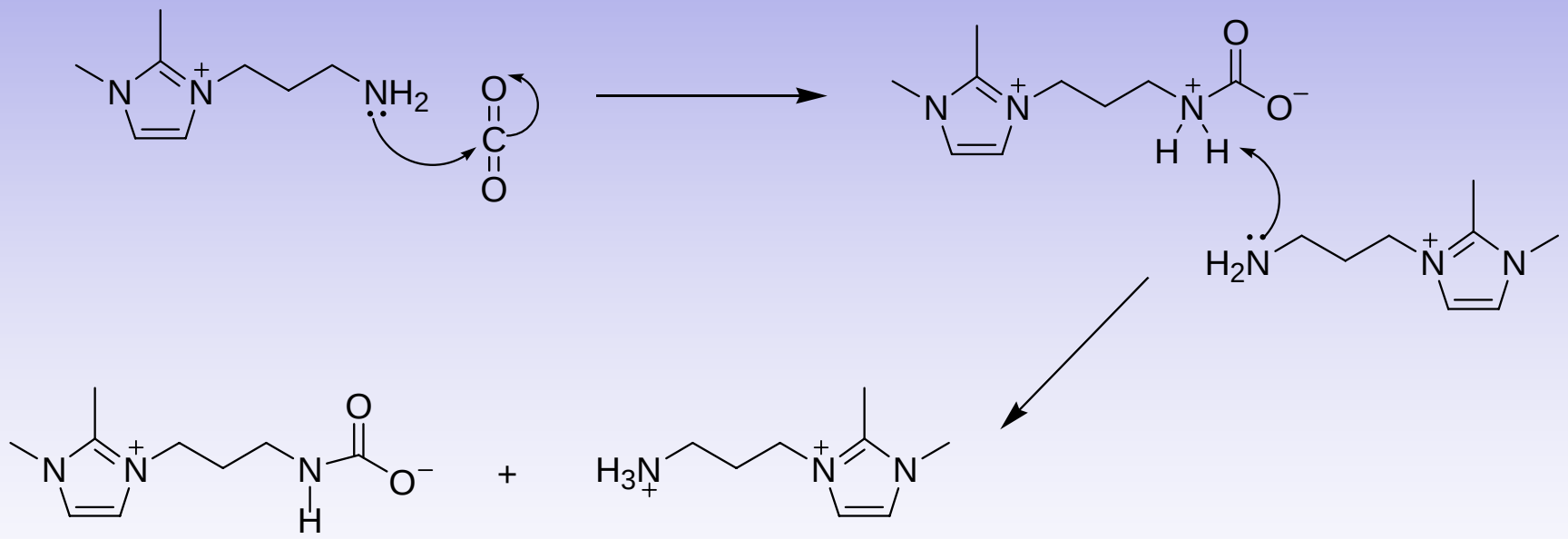
Experimental setup: Gravimetric microbalance

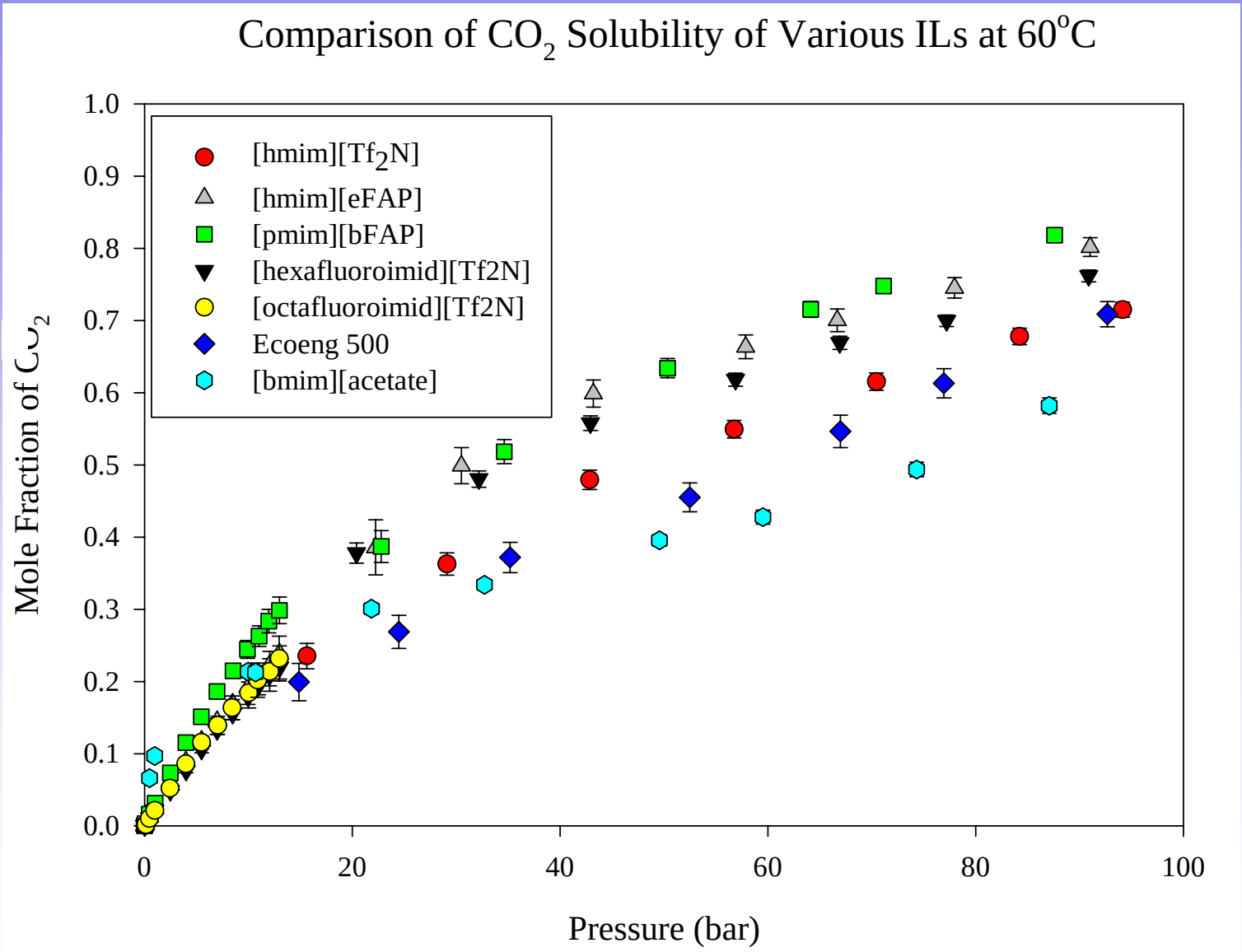


Characterization

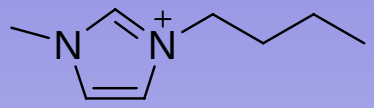
- ^{1}H and ^{13}C NMR
- Br^- and NH_4^+ ion-selective electrode
- ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) for Ag^+
- Karl-Fisher Titration for water content

Carbamate Formation

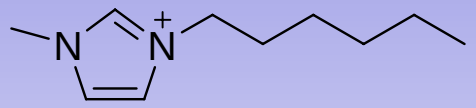



Comparison of CO_2 Solubility of Various ILs at 60°C
Mole Fraction of CO_2
Pressure (bar)
[hmim][Tf2N]
[hmim][eFAP]
[pmim][bFAP]
[hexafluoroimid][Tf2N]
[octafluoroimid][Tf2N]
Ecoeng 500
[bmim][acetate]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
20
40
60
80
100

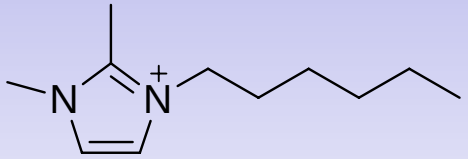
Cations



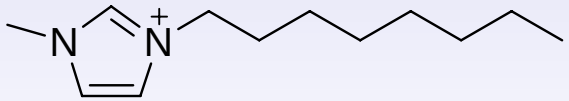
[bmim]



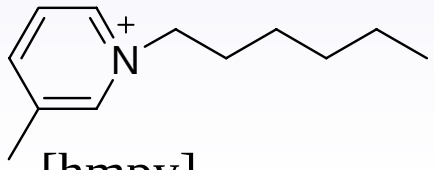
[hmim]



[hmmim]

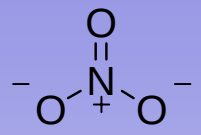


[omim]

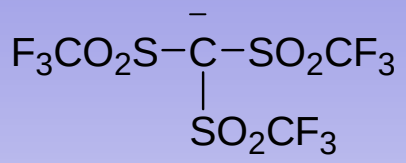


[hmpy]

Anions

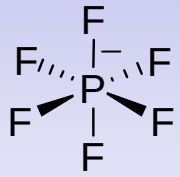


[NO_3]



[methide]

[BF_4]



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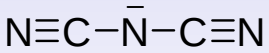
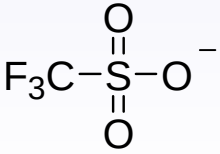
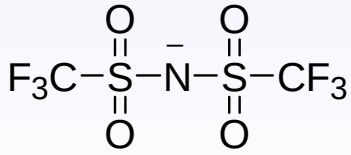


[DCA]



[TfO]



[TF_2N]