A potential ionic liquid for CO_2-separating membranes:

selection and gas solubility studies

Sona Raeissi
Astrid Schilderman
Cor J. Peters
Physical Chemistry & Molecular Thermodynamics
Delft University of Technology

GCEP Research Symposium 2006

September 19

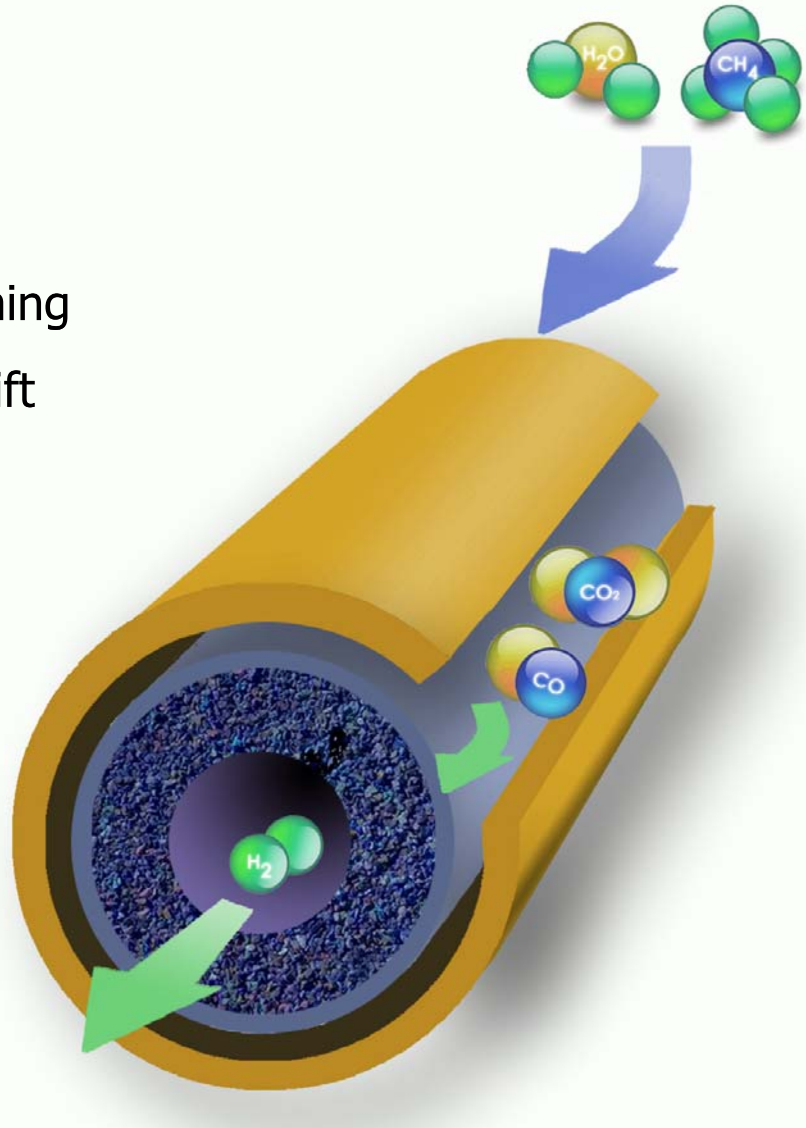
Production of hydrogen from fossil fuels

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ steam reforming

$CO + H_2O \leftrightarrow CO_2 + H_2$ water gas shift

Separation-enhanced membrane reactor

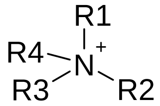
- eliminate two water gas shift reactors
- higher conversion efficiencies
- lower reaction temperature



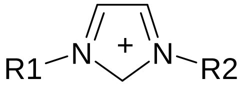
Ionic liquids

Ionic liquids are organic salts consisting of cations and anions.
They are usually liquid at room temperature.

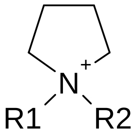
Common cations:



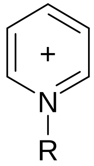
quaternary ammonium



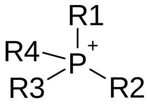
imidazolium



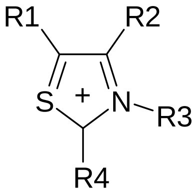
pyrrolidinium



pyridinium



tetra alkylphosphonium



thiazolium

Common anions:

BF_4^-
PF_6^-
$Al_2O_7^-$
$CF_3SO_3^-$
$CF_3CO_2^-$
$N(CF_3SO_2)_2^-$

Advantages of Ionic Liquids

- **Nonvolatile**
- Good solvent power for both polar and nonpolar compounds
- Suitable density and viscosity
- Thermally stable
- Nonflammable
- Wide liquidus range
- Possible to engineer ionic liquids of suitable properties by combining appropriate anions, cations, and varying their chain lengths

Ionic liquid selection criteria for CO_2-separation membranes

- High solubility for CO_2
- Low solubility for H_2
- High solubility for CO is favourable
- Thermal stablity at $T \geq 150°C$
- Workable viscosity

What's known and what's not?

Solubility data of various gases in ionic liquids are still greatly lacking.

Even those that are available are mostly at low temperatures & pressures and in the form of Henry's constants:

$$H = \lim_{x \to 0} \frac{P}{x}$$

Henry's constant of gases at atmospheric P and T

Ionic Liquid	$[H_2]$, MPa [a]	[CO], MPa [b]	$[CO_2]$, MPa [c,d]
$[emim][BF_4]$	—	667	—
$[bmim][BF_4]$	580	337	5.65
$[hmim][BF_4]$	570	161	—
$[bmim][PF_6]$	660	327	6.18
$[bmim][SbF_6]$	490	201	—
$[bmim][CF_3CO_2]$	490	191	—
$[emim][Tf_2N]$	—	118	3.9
$[bmim][Tf_2N]$	450	95	3.7
$[hmim][Tf_2N]$	—	76	3.5

Ref: [a] Dyson et al. (2003), [b] Ohlin et al. (2004), [c] Cadena et al. (2004), [d] Baltus et al. (2004)

Thermal stability of ionic liquids

Ionic liquid	Temperature onset for decomposition (dried), °C
[bmim][Cl]	254
[bmim][I]	265
[emim][BF_4]	412
[bmim][BF_4]	360/403
[emim][PF_6]	375
[bmim][PF_6]	349
[emim][CF_3CO_2]	150
[emim][Tf_2N]	440/455
[pmim][Tf_2N]	452
[bmim][Tf_2N]	439

ref: Huddleston et al. (2001)

Viscosity decreases in the order $Cl^- > [PF_6]^- > [BF_4]^- > [Tf_2N]^-$

Ionic Liquid	Viscosity at 25°C, cp
[hmim][Cl]	716
[emim][BF_4]	43
[bmim][BF_4]	233
[hmim][BF_4]	314 at 20°C
[bmim][PF_6]	450
[hmim][PF_6]	585
[bmim][CF_3CO_2]	73
[emim][Tf_2N]	28
[bmim][Tf_2N]	52
[hmim][Tf_2N]	—

ref: Huddleston et al. (2001)

GCEP

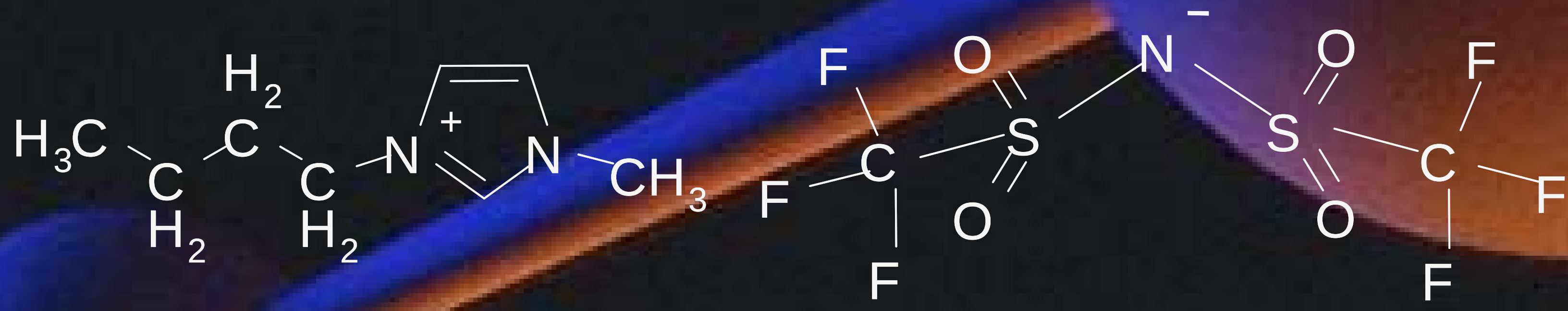
TU Delft

But which member of the Tf_2N family?

Ionic liquid	Thermal stability		Viscosity (cp)	Solubility as Henry's Constant, MPa			Commercial availability	
	Short term degradation onset temp. (°C)	Long term stability		H_2	CO	CO_2	purity	Price$ per 5g
mmim[Tf_2N]					134		-	-
emim[Tf_2N]	400-455		28@25°C		118	3.9	>97%	317
pmim[Tf_2N]	452					3.7		
bmim[Tf_2N]	422-439	Stable At 200°C After 10h	52-69 @25°C	450	95	3.7	>98%	262
hmim[Tf_2N]					76	3.5	-	-
omim[Tf_2N]					67	3.0	-	-
emmim[Tf_2N]			88@25°C			4.0	-	-
bmmim[Tf_2N]			97@25°C	380			-	-

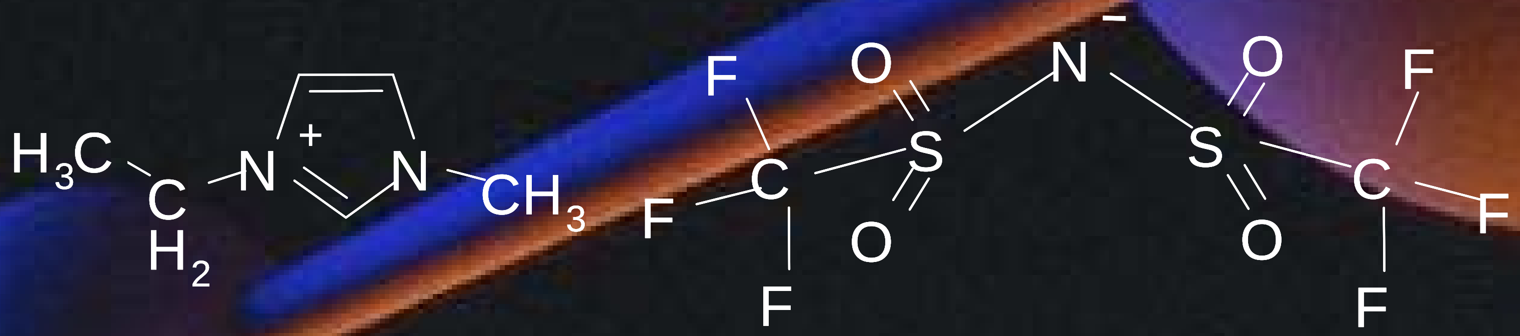
GCEP

TU Delft



Abbreviation: [bmim][Tf_2N]

1-butyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide

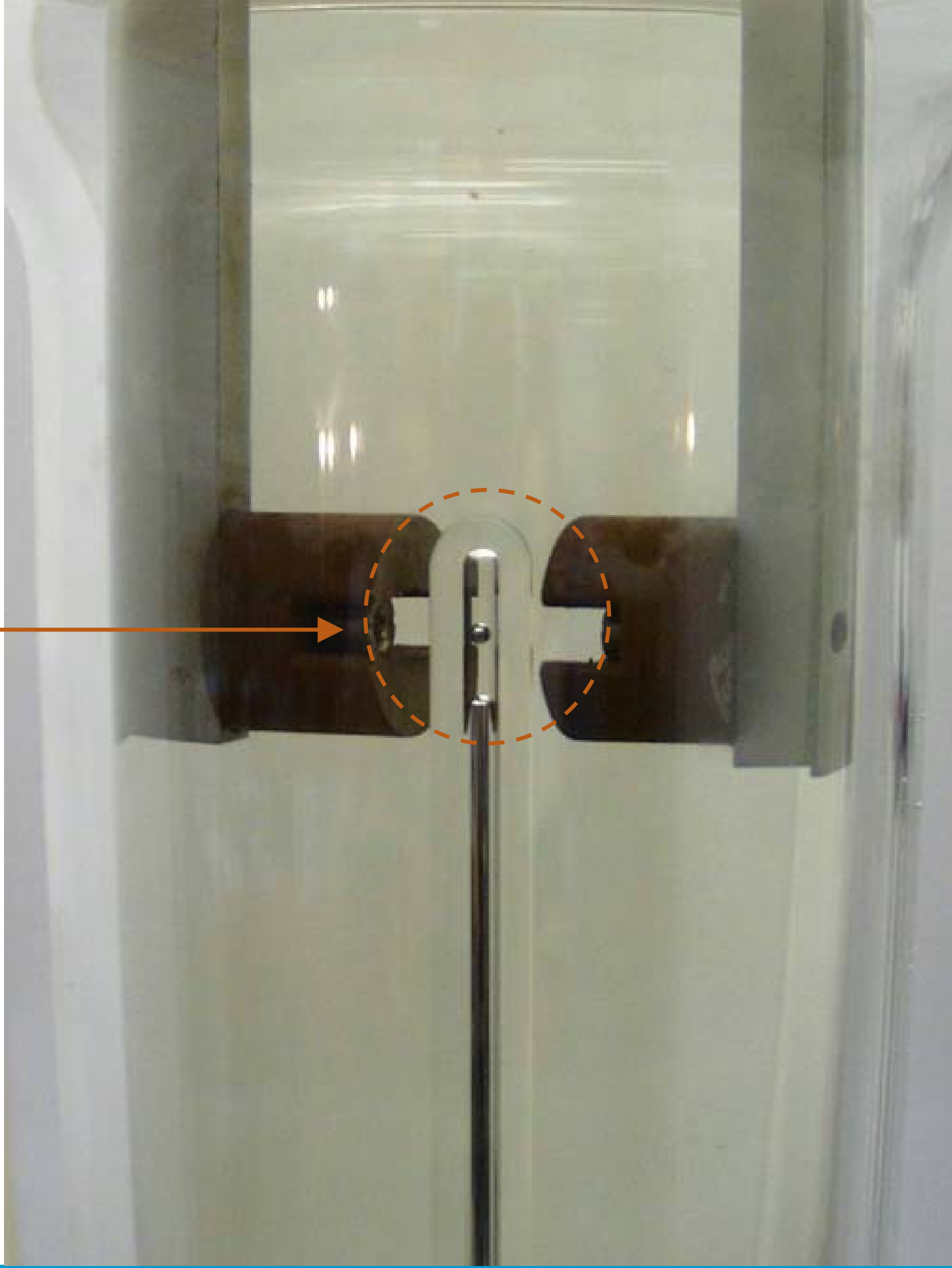


Abbreviation: [emim][Tf_2N]

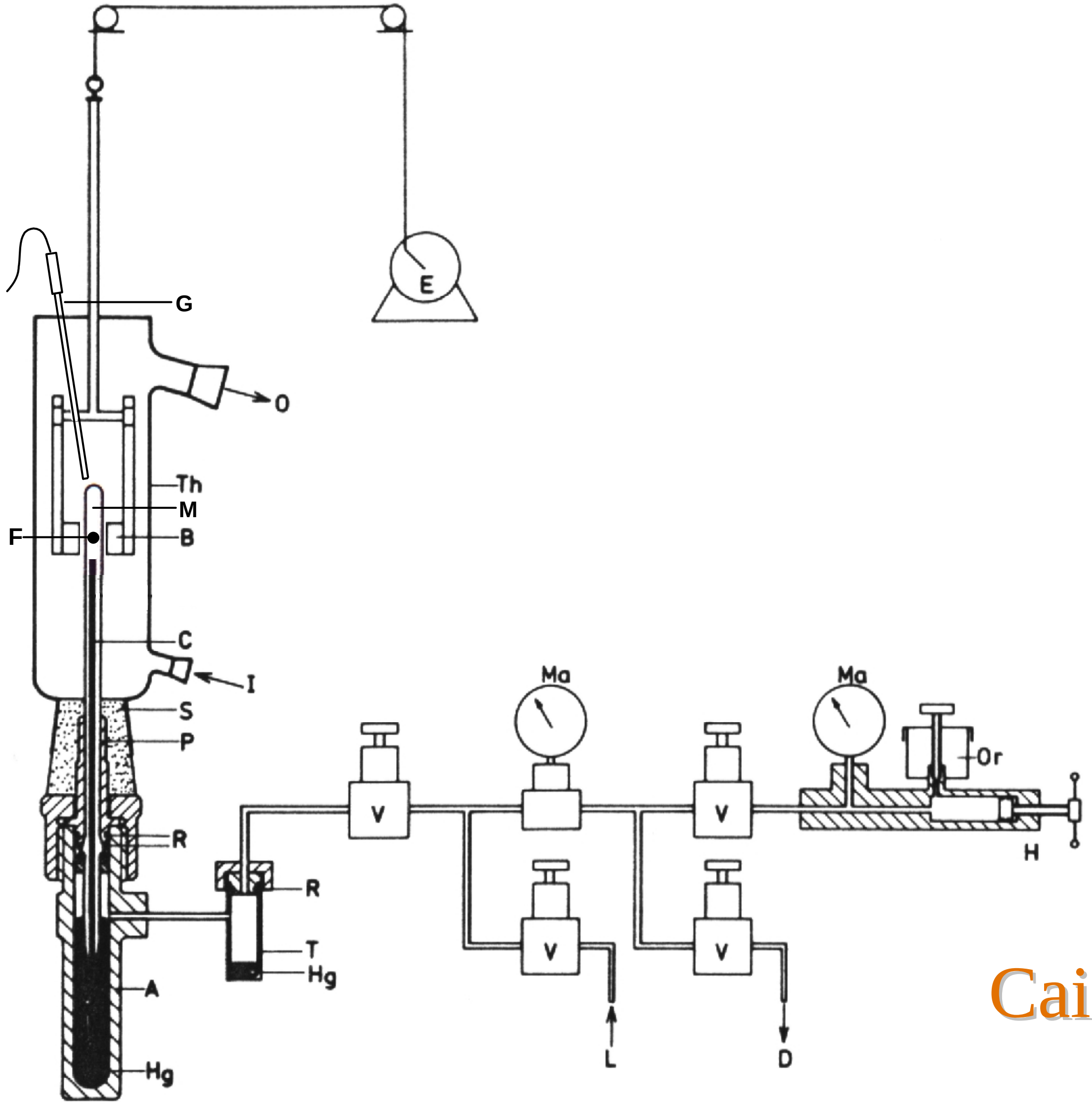
1-ethyl-3-methyl-imidazolium-bis-(trifluoromethylsulphonyl) imide

Cailletet Tube

Sample mixture



Overview of the Cailletet Apparatus



Cailletet Equipment

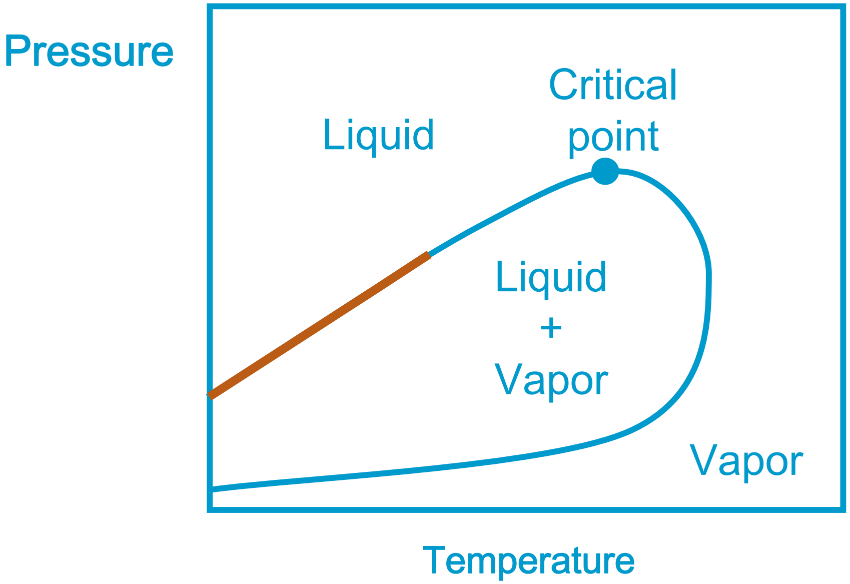
Cailletet Equipment

The number of phases can be observed visually

Adjustable Pressure and/or Temperature

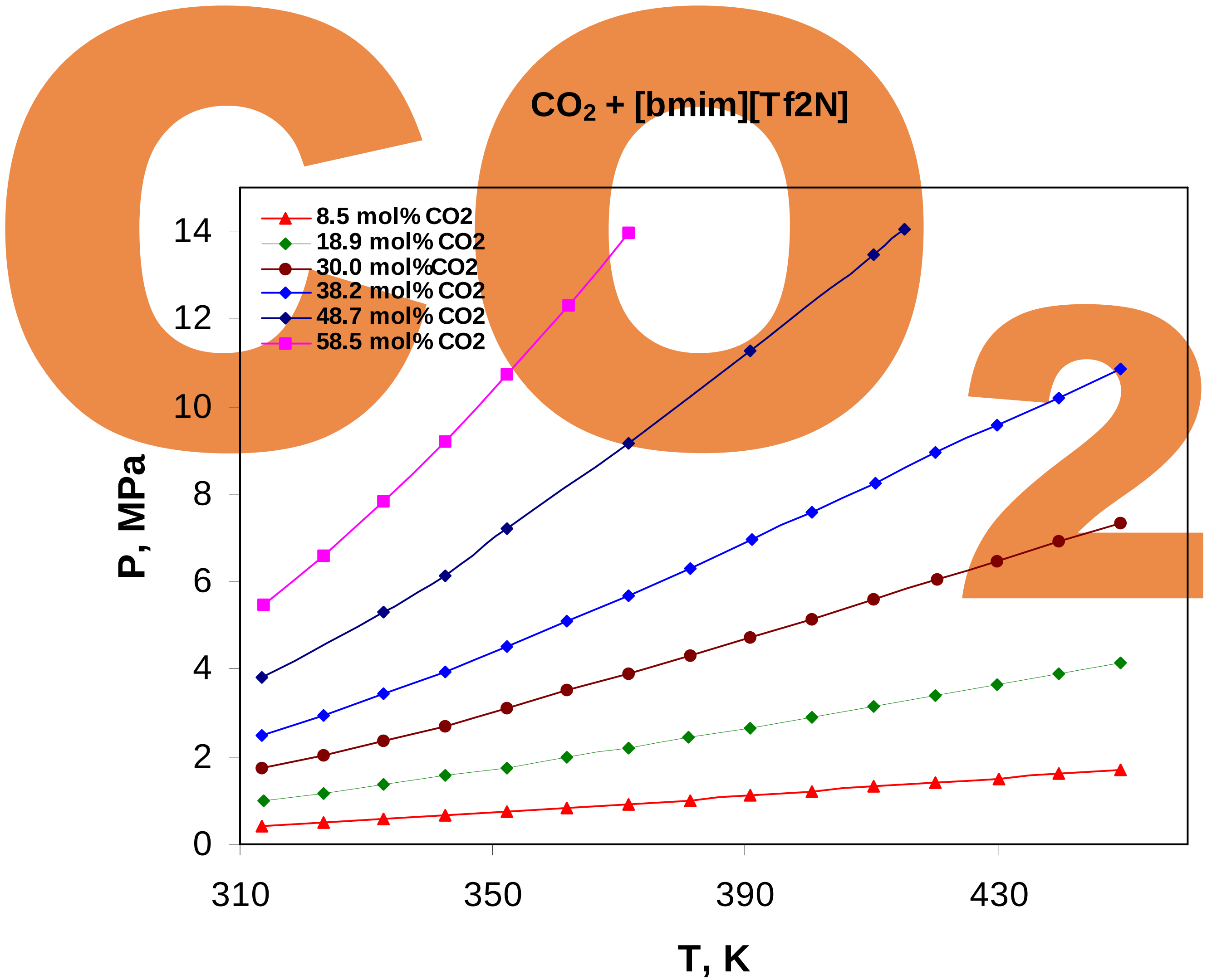
Measuring Range	0.3 - 15 [MPa]	250 - 450 [K]
Accuracy	0.03% [MPa]	0.02 [K]

Phase envelope of a mixture of constant overall composition



Experimental Results for the ionic liquid:

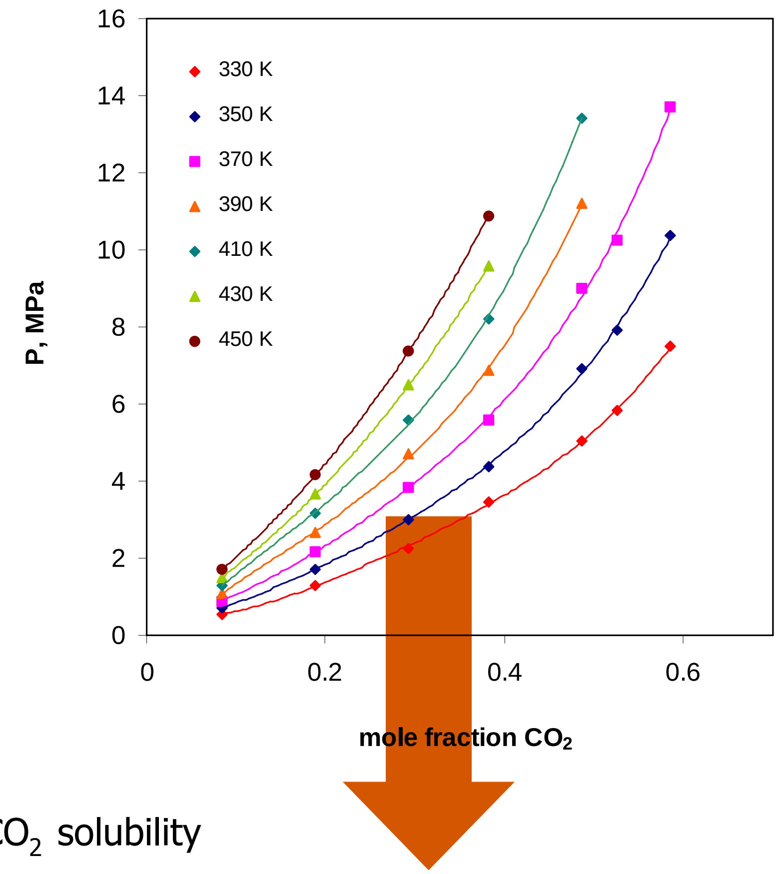
[bmim][Tf_2N]



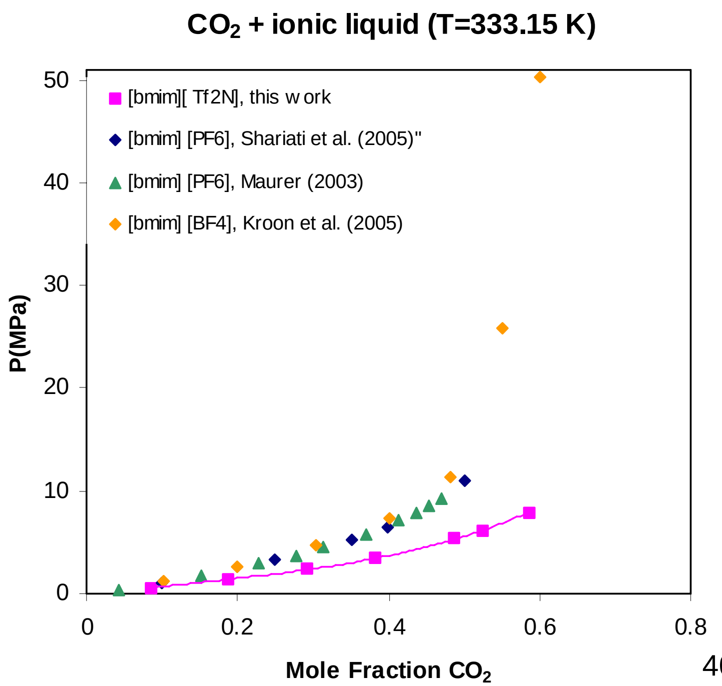
GCEP

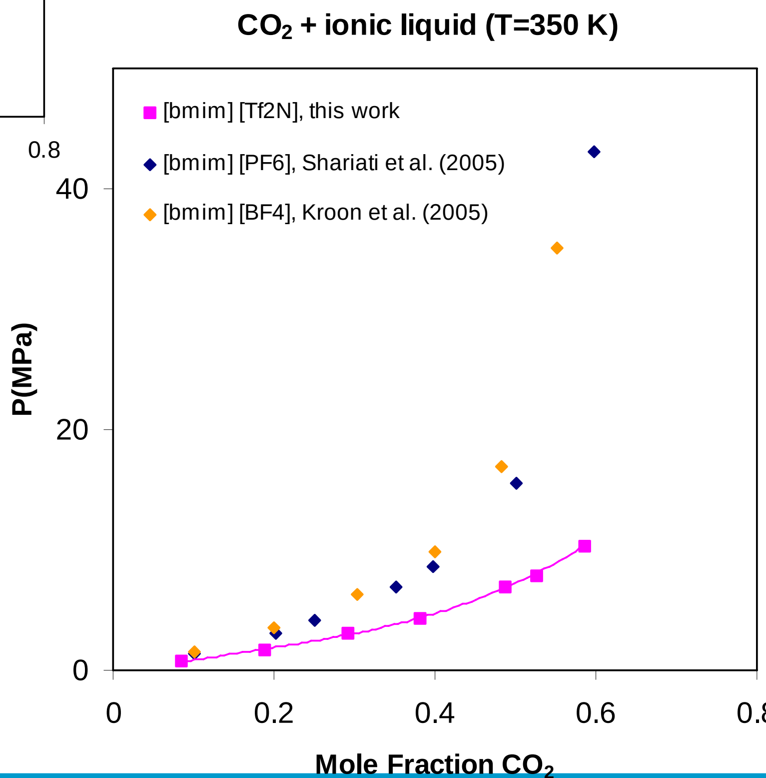
TU Delft

CO_2 + [bmim][Tf_2N]



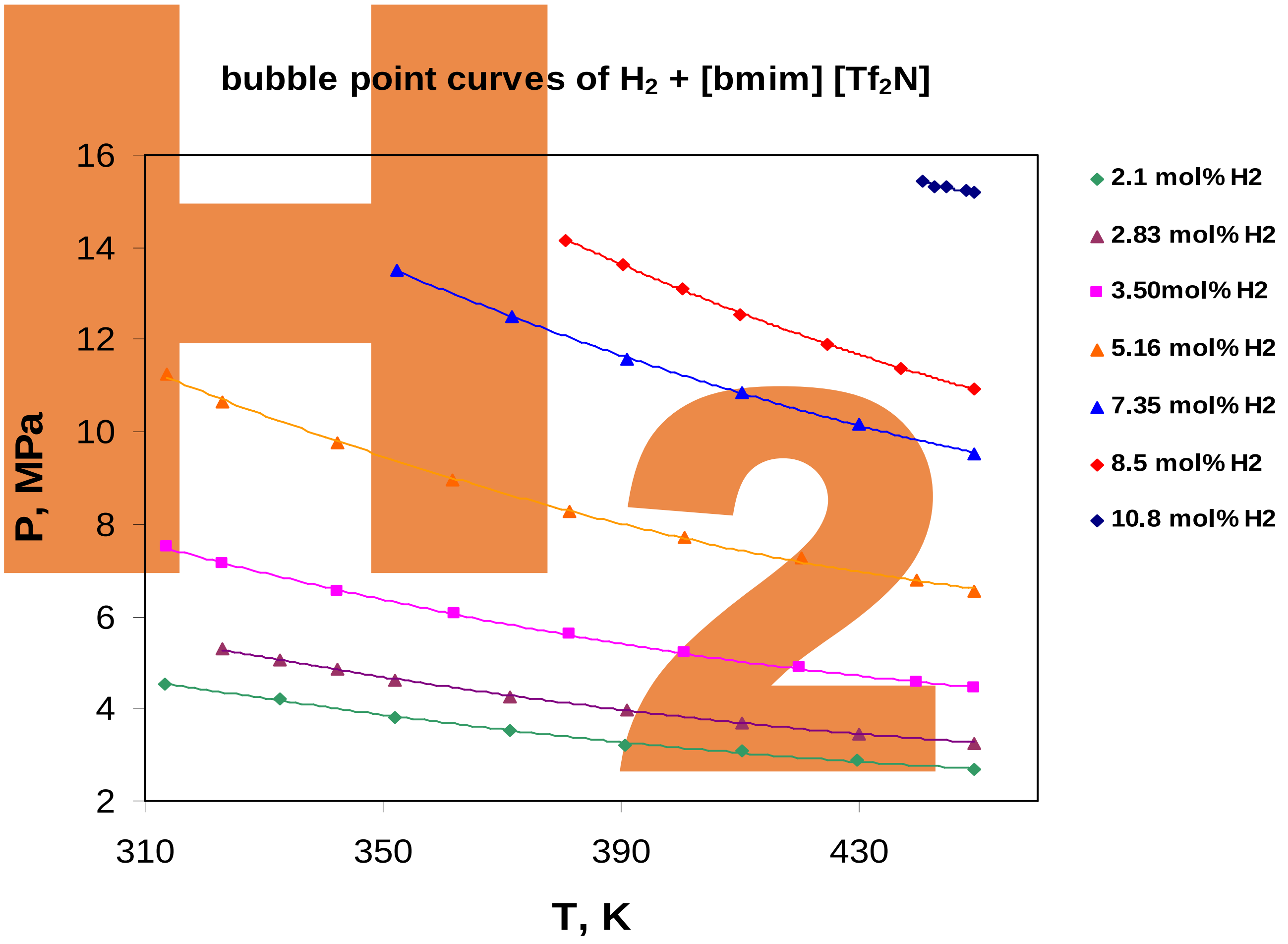
- Very high CO_2 solubility
- Strong dependence of solubulity on T and P
- Nonideal system: extrapolating from Henry's law can lead to serious errors
- Diverging region should be avoided





GCEP

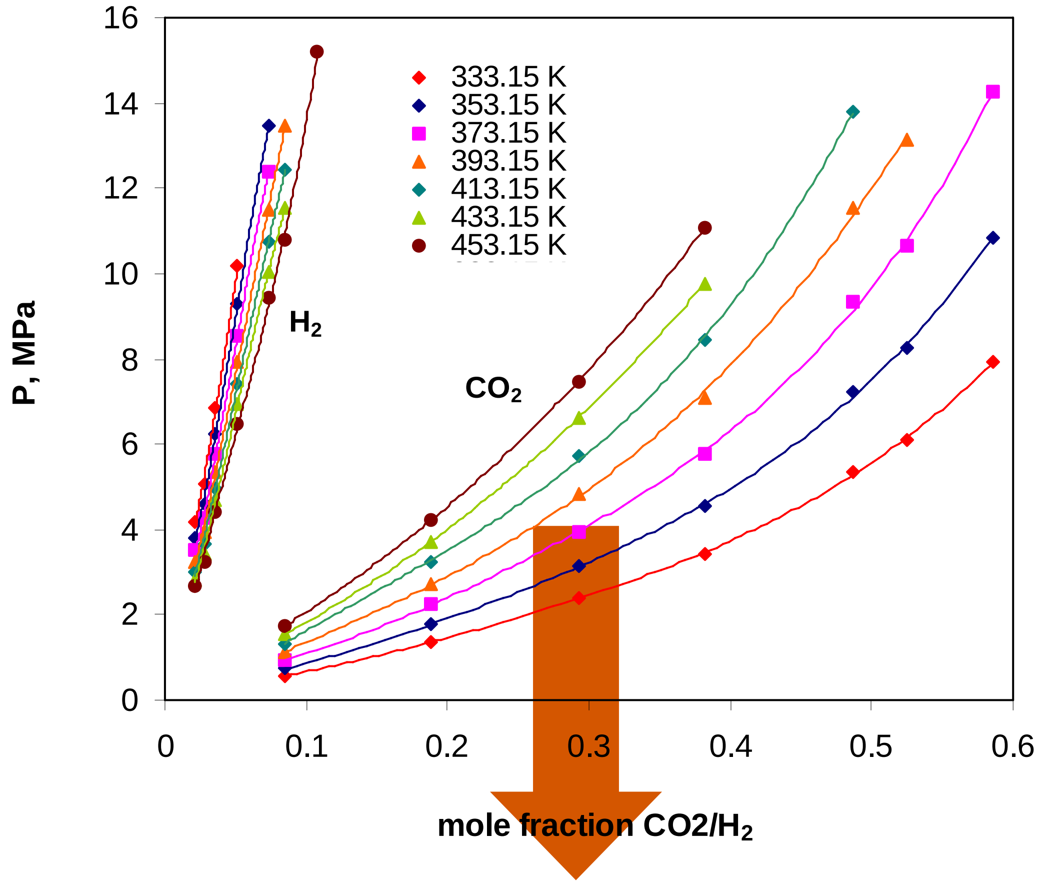
TU Delft



GCEP

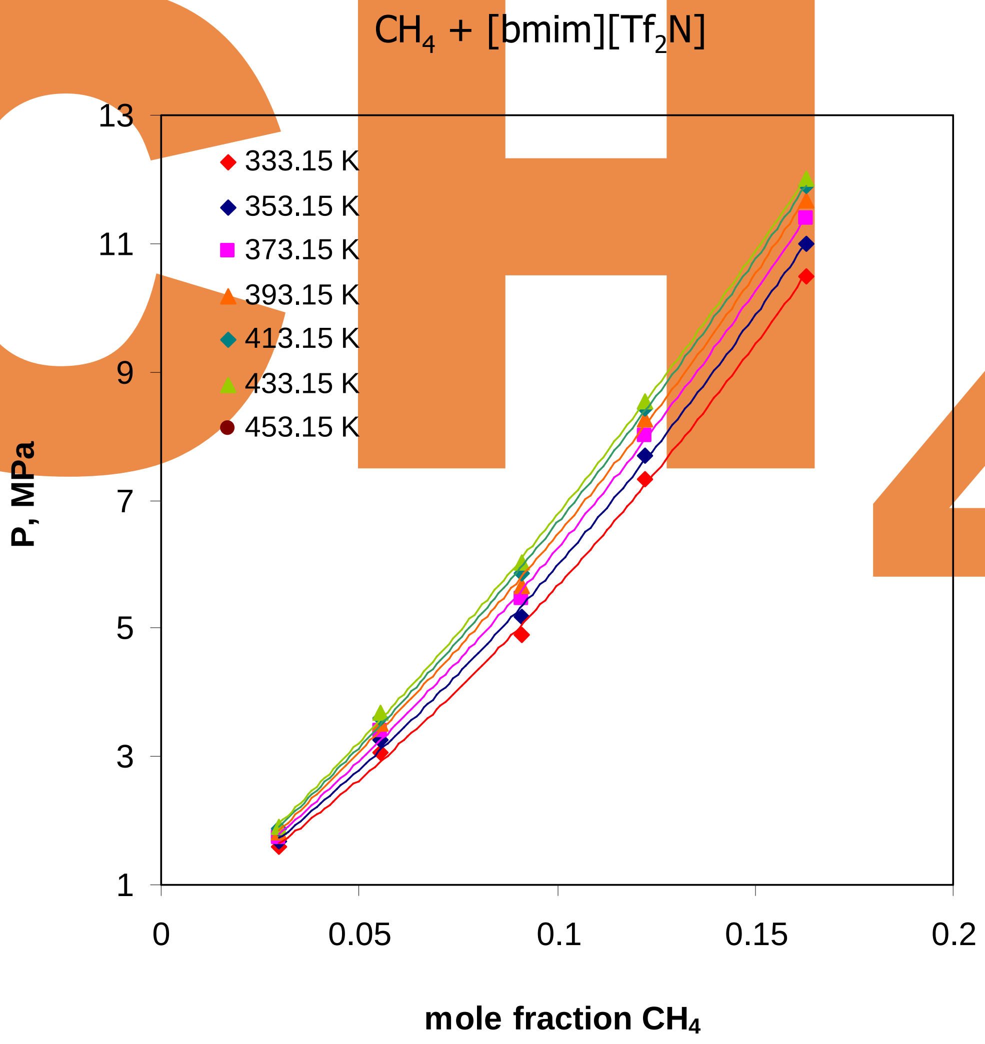
TU Delft

comparison of CO_2 and H_2 solubilities in [bmim][Tf2N]



- H_2 solubility one order of magnitude lower than CO_2 solubility, hence separation is possible.
- Solubility ratios vary significantly (5<CO_2/H_2<15) depending on T and P

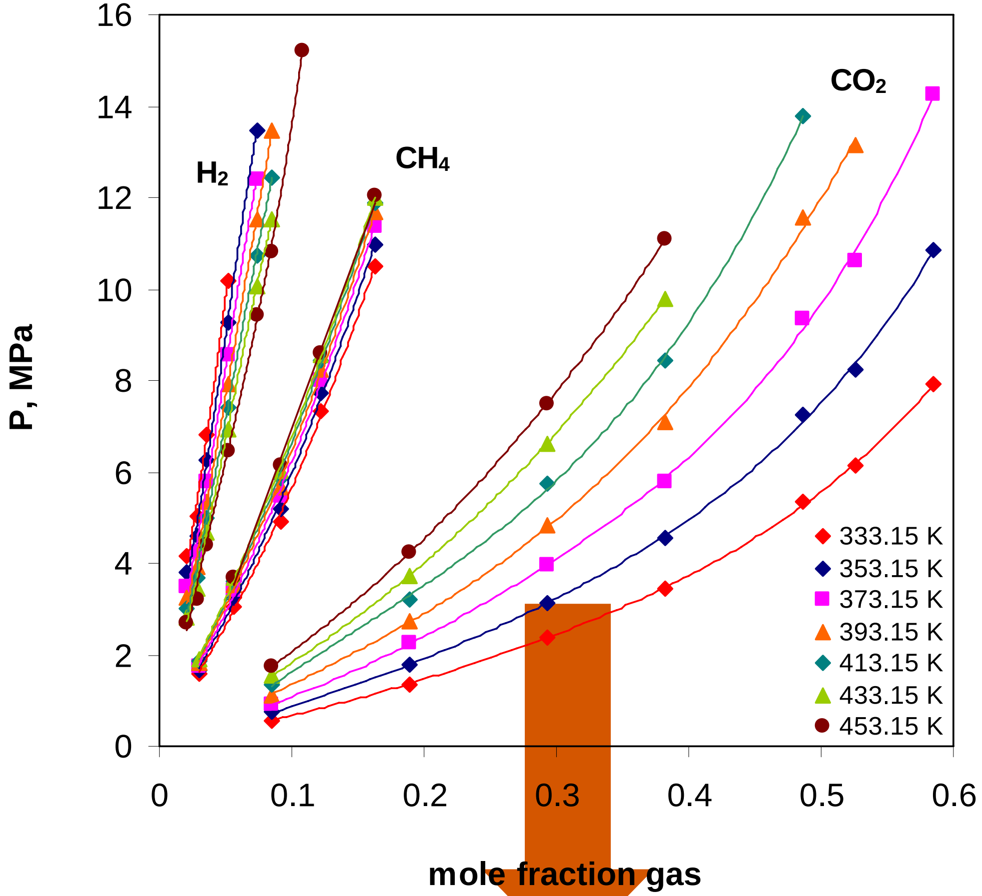
CH_4



GCEP

TUDelft

Gas solubilities in [bmim][Tf_2N]

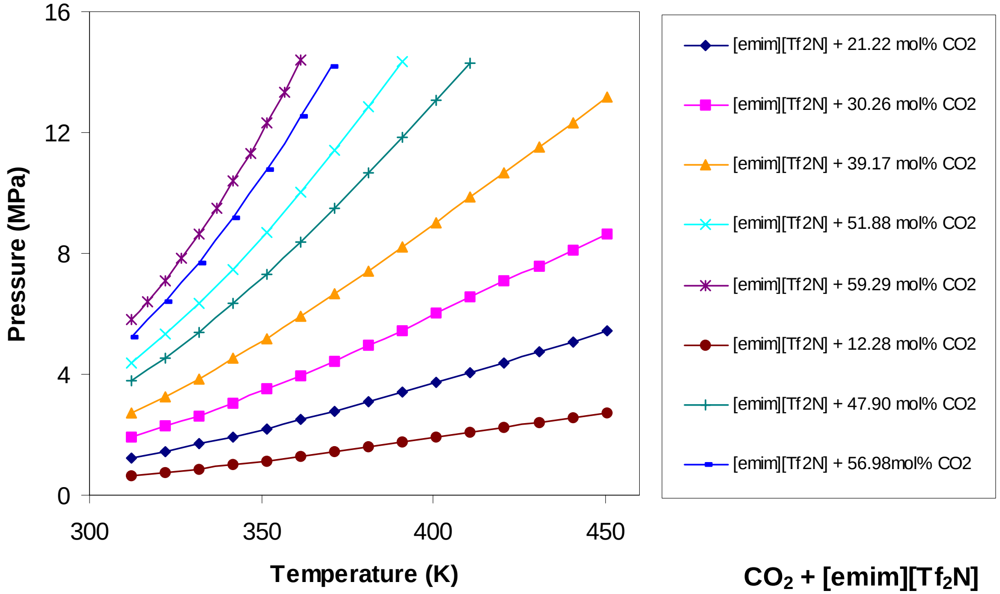


- The curvature in the CO_2 solubilities & the linear solubilities of H_2 and CH_4 suggest an optimal mid-range pressure for maximum separation efficiency.
- The opposite trends of solubilities of CO_2 and H_2 with temperature suggest operation at lowest possible temperature for best separation.

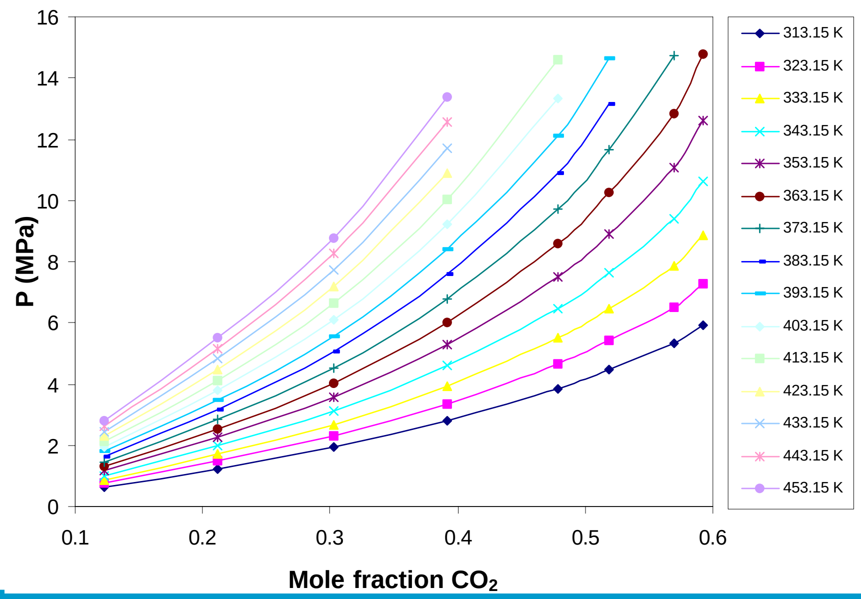
Experimental Results for the ionic liquid:

[emim][Tf_2N]

Bubble point lines for CO_2 + [emim][Tf_2N]



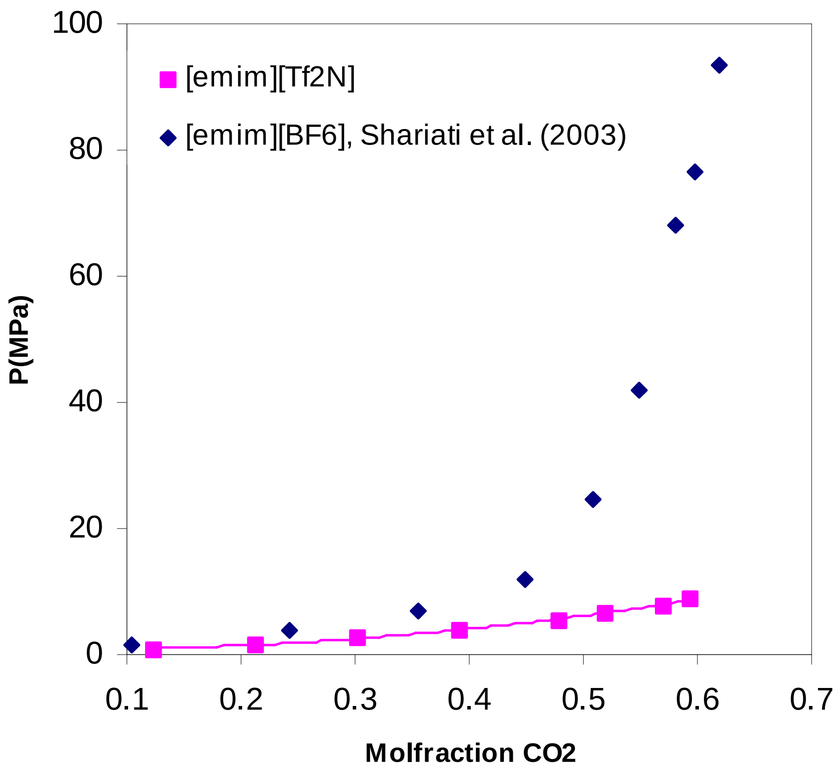
CO_2 + [emim][Tf_2N]



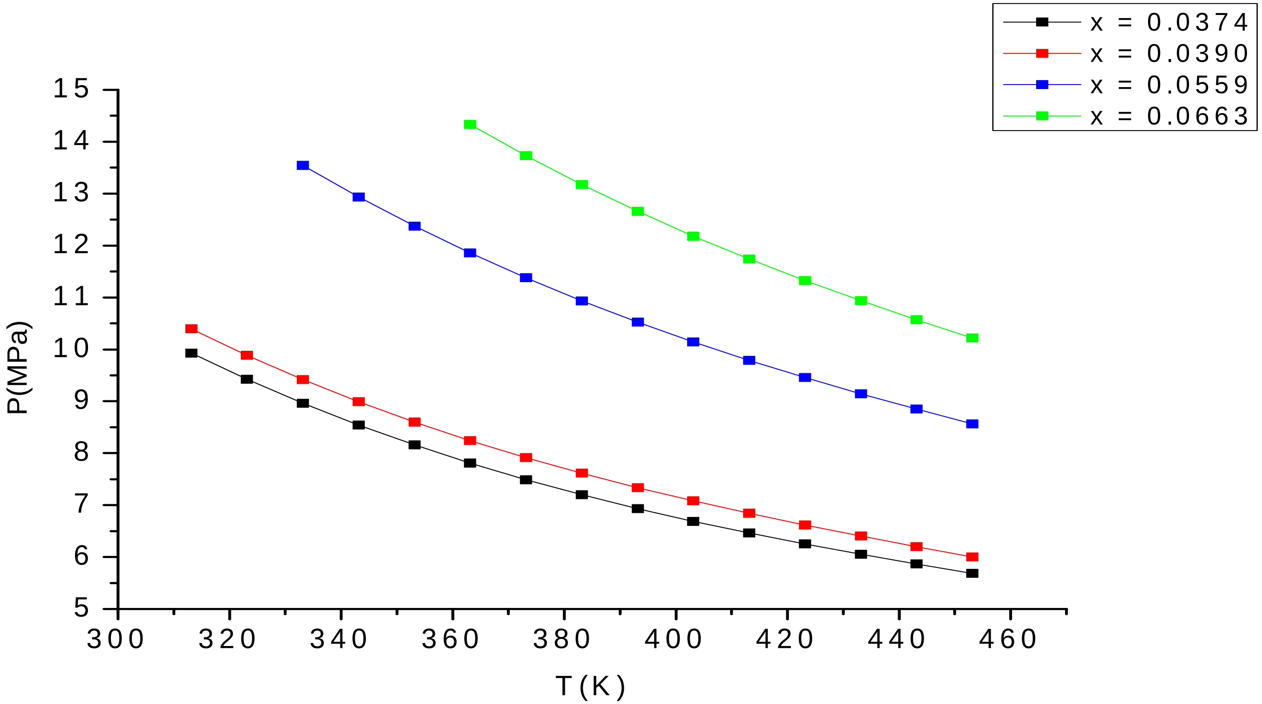
GCEP

TU Delft

CO_2 + ionic liquids with the [emim] cation at T=333.15 K



Bubble point curves of H_2 + [emim][Tf_2N]



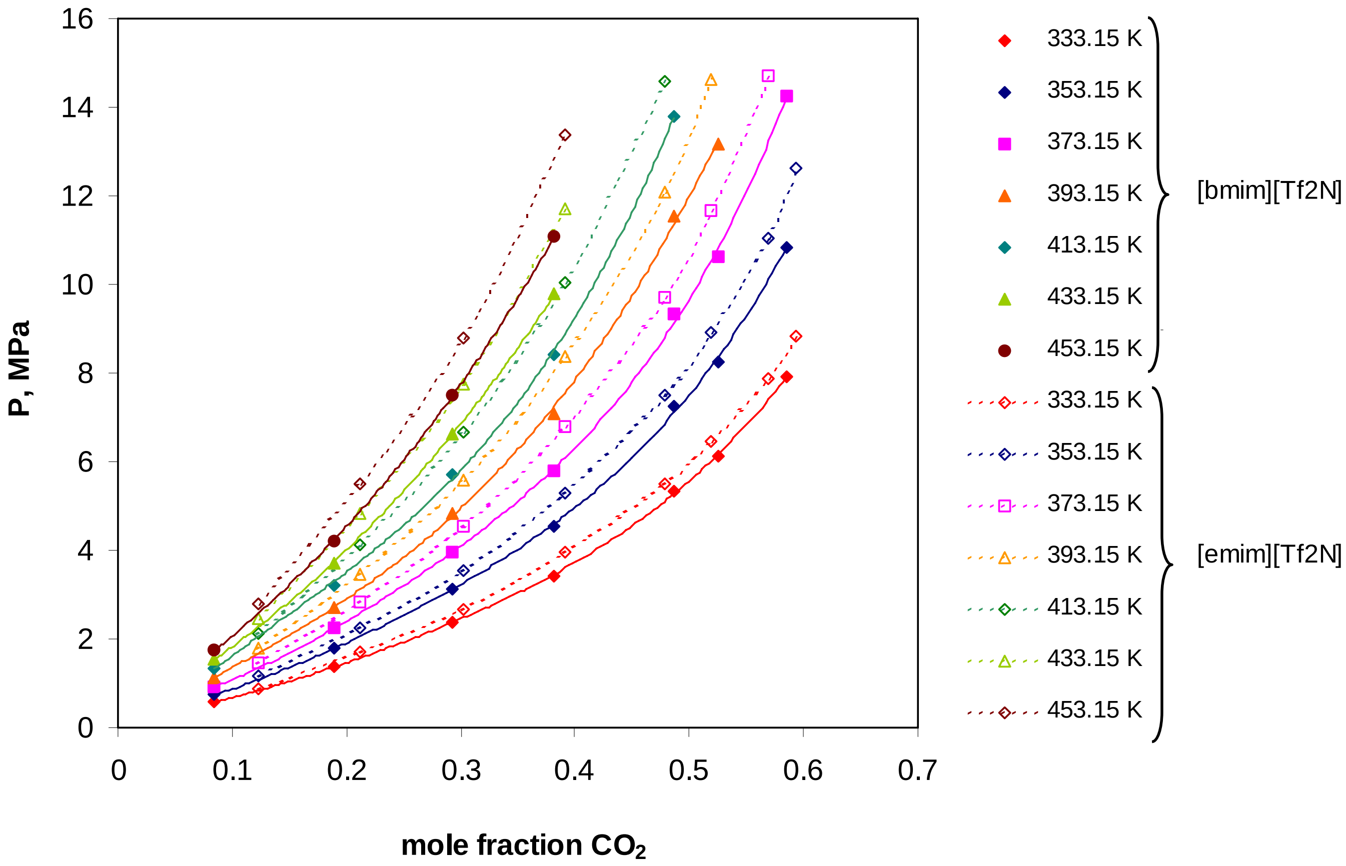
GCEP

TU Delft

Comparison of

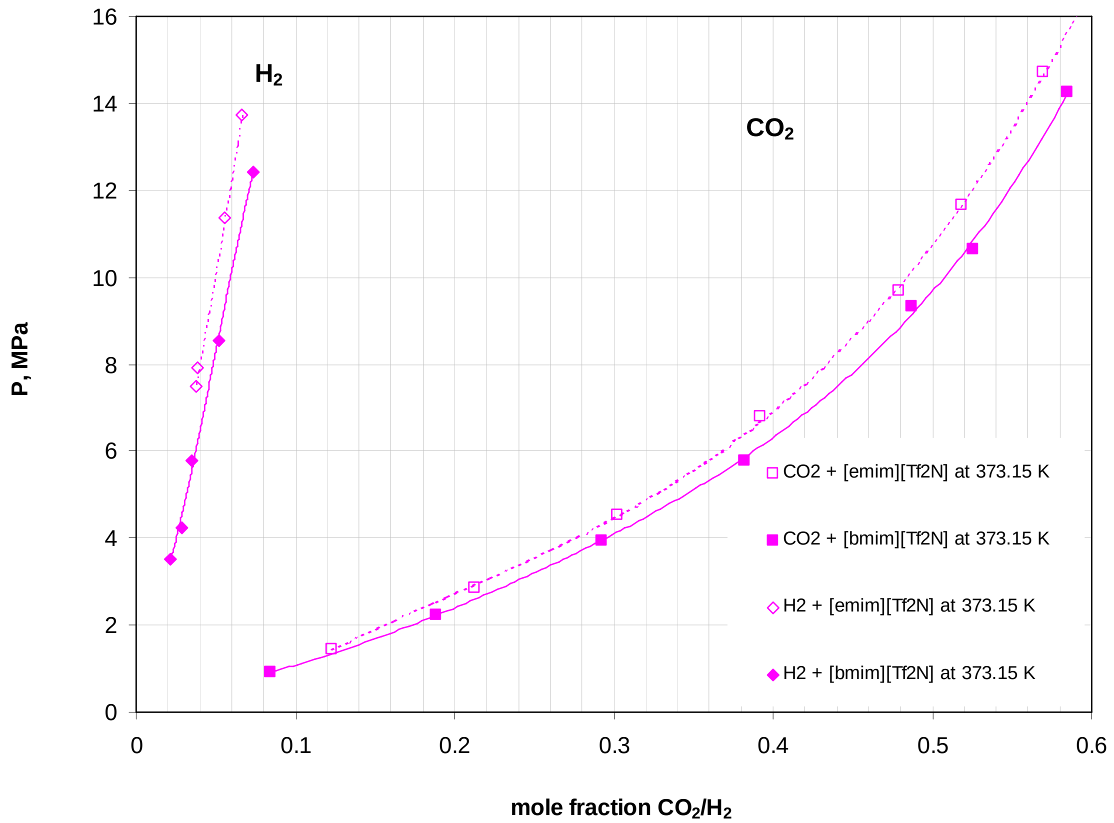
[emim][Tf_2N] and [bmim][Tf_2N]

Comparison of [emim][Tf2N] and [bmim][Tf2N]



GCEP

TUDelft



At 373.15 K and P=10 MPa:

[emim][Tf_2N]	CO_2/H_2 = 9.8	= 12.4%
[bmim][Tf_2N]	CO_2/H_2 = 8.6	

In addition, the lower viscosity of [emim][Tf_2N] allows for faster kinetics

Conclusions

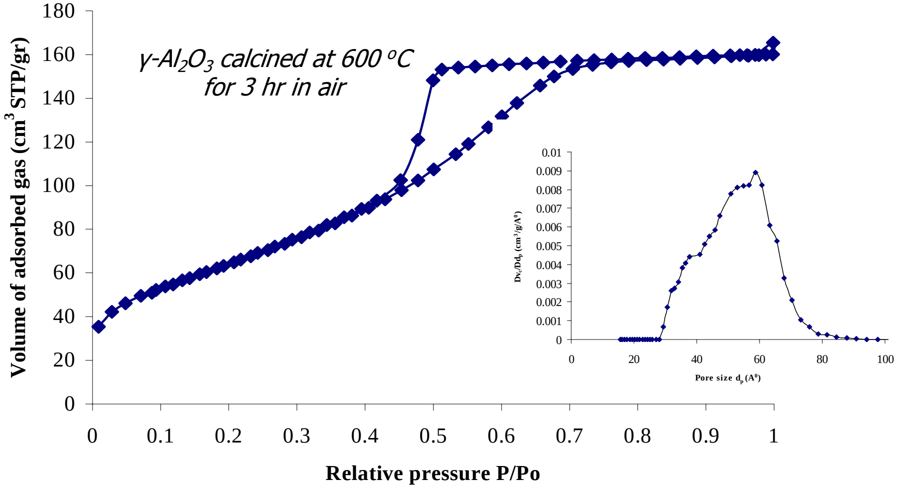
- Two ionic liquid have been selected for possible use in CO_2-separating membranes.
- Preliminary solubility measurements seem to indicate favorable outcome, ranging between $5<CO_2/H_2<15$.
- Solubility ratios vary significantly depending on T and P.
- CO_2-H_2 separation improves as temperature decreases.
- CO_2-H_2 separation improves as pressure increases but can deteriorate at very high pressures.
- [bmim][Tf_2N] has slightly higher solubility for CO_2 than [emim][Tf_2N].
- However, the CO_2/H_2 selectivity of [bmim][Tf_2N] is less than [emim][Tf_2N].

Remaining ...

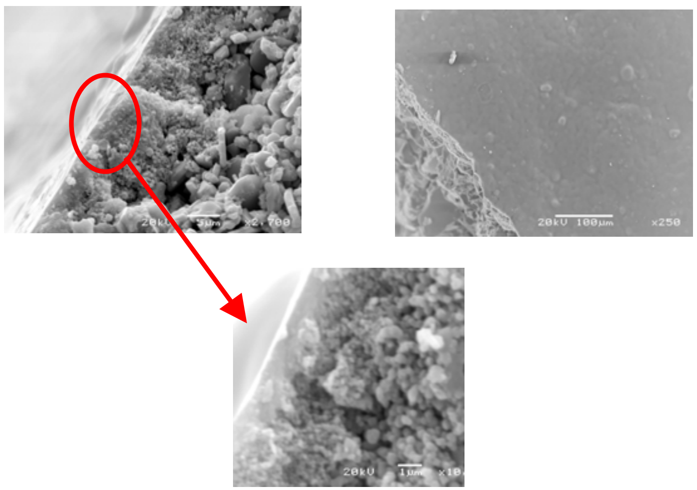
- The solubility of CO in the selected ILs
- The effect of water on solubilities
- Ternary and multicomponent phase behavior
- Thermodynamic modelling for inexpensive predictions
- ....

Development of Membrane Materials for Advanced Reactors for Carbon-Free Fossil Fuel Conversion

Synthesis of appropriate materials for further modification by Atomic Layer Deposition technique



Nitrogen adsorption-desorption isotherm and the respective pore size distribution for unsupported γ-Al_2O_3 thin films



Scanning electron micrograph of cross section and surface of a supported γ-Al_2O_3 membrane