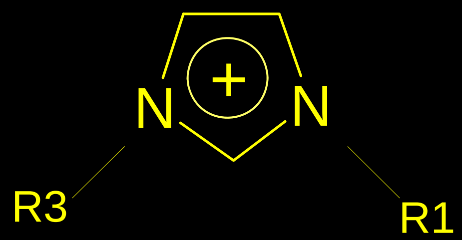
Solubilities of Gases in the Ionic Liquids

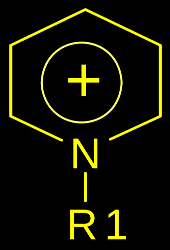
by Won-Young Choi
Thermodynamics & Properties lab.
Korea University

Introduction

- What is the Ionic Liquids?
  - Organic salts composed of cations and anions around room temperature
  - First Ionic Liquid reacted with water to form highly corrosive compounds
    - N-ethylpyridinium bromide-aluminium chloride melt (Hurley et al., 1951)
  - Two main groups of ionic liquid
    - Water and air stable



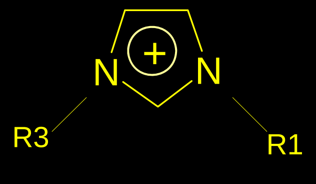
Imidazolium

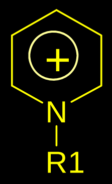


Pyridinium

Structure of Ionic Liquids

- Cations
  - Based on Imidazolium, Pyridinium (organic compounds)





- Anions
  - Inorganic compounds

$[BF_4]^-$ $[CF_3CO_2]^-$ $[PF_6]^-$ $[NO_3]^-$ $[EtSO_4]^-$

- Schematic of the structure of [bmim]$[PF_6]$

+ $[PF_6]^-$

Preparation of Ionic Liquids

- Imidazolium based Ionic Liquids
  - Reaction of N-alkylimidazole, RIm,
    with alkyl salts (R´X) in appropriate organic solvents

(1) X^- is the anion of interest

$$RIm + R'X \longrightarrow RR'Im^+X^-$$

(2) Fist step, alkylimidazolium halides are synthesized

$$RIm + R'X' \longrightarrow RR'Im^+X'^-$$

X´=Cl, Br, I

(3) Anion exchange corresponding acids of their salts

$$RR'Im^+X'^- + MX \longrightarrow RR'Im^+X^- + MX'$$

§ The choice of cation M is important §

Properties

- Physical Properties
  - Melting point (-96°C ~)
    - Melting point is lowered as increasing length of alkyl chain in cations
    - The increasing disruption of crystal packing overrides increased van der Waals interactions between the larger components.
  - Density
    - 1.1 ~ 1.6 g/cm^3 at ambient temperature (291~303K)
    - The compounds of bulky, and therefore, weakly coordinating anions such as $CF_3(CF_2)_3SO_3^-$ and $(CF_3SO_2)_3C^-$ possess relatively high densities regardless of counter ions.

Properties

- Viscosity
  - Several tens to hundred times that of water at room temperature
  - Longer alkyl chains of cation makes the liquid more viscous.
  - Structure and basicity of anion affects the viscosity.
    - The decrease of the size of anion decreases the van der Waals interaction but increases the electrostatic interaction through hydrogen bonding.

Application

- Non-volatile, negligible vapor pressure

  – Green chemical solvents
    - Increasing limitations on volatile organic emissions
    - ILs are possible to replace the solvents

  – Distillation with poorly volatile or thermally labile products

  – Extraction using supercritical CO_2
    - Don’t have a cross-contamination
    - Supercritical CO_2 extraction achieved greater than 98% solute recovery for several of the organics

(Blanchard et al, I&EC, 2001; Nature, 1999)

- Measuring the recovery rates of aromatic and aliphatic solutes from [bmim][PF_6]

- This work has shown that CO_2 can completely extract a wide array of organic solutes from an ionic liquid.

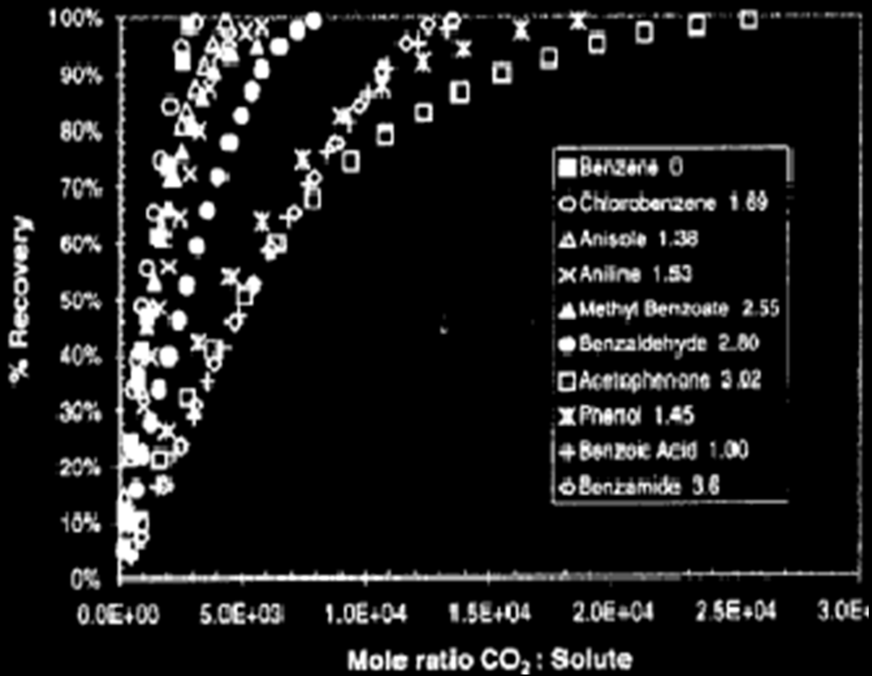


Figure 1. Extraction of aromatic solutes from [bmim][PF_6] with $SCCO_2$ at 40 °C and 138 bar

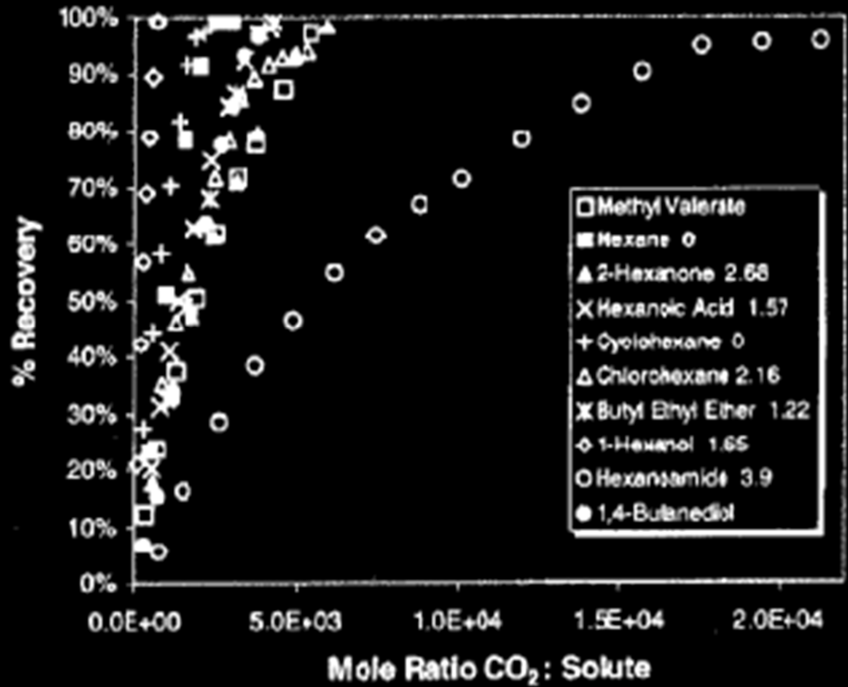


Figure 2. Extraction of aliphatic solutes from [bmim][PF_6] with $SCCO_2$ at 40 °C and 138 bar

Application

– Good solvent

  - High solubility and selectivity with organic, inorganic, organometallic compounds
  - Reaction solvent
  - Used to the liquid-liquid extraction process

– Catalysis

  - Fiedel-Crafts alkylations, Diels-Alder reaction , hydrogenation , hydroformylation etc.

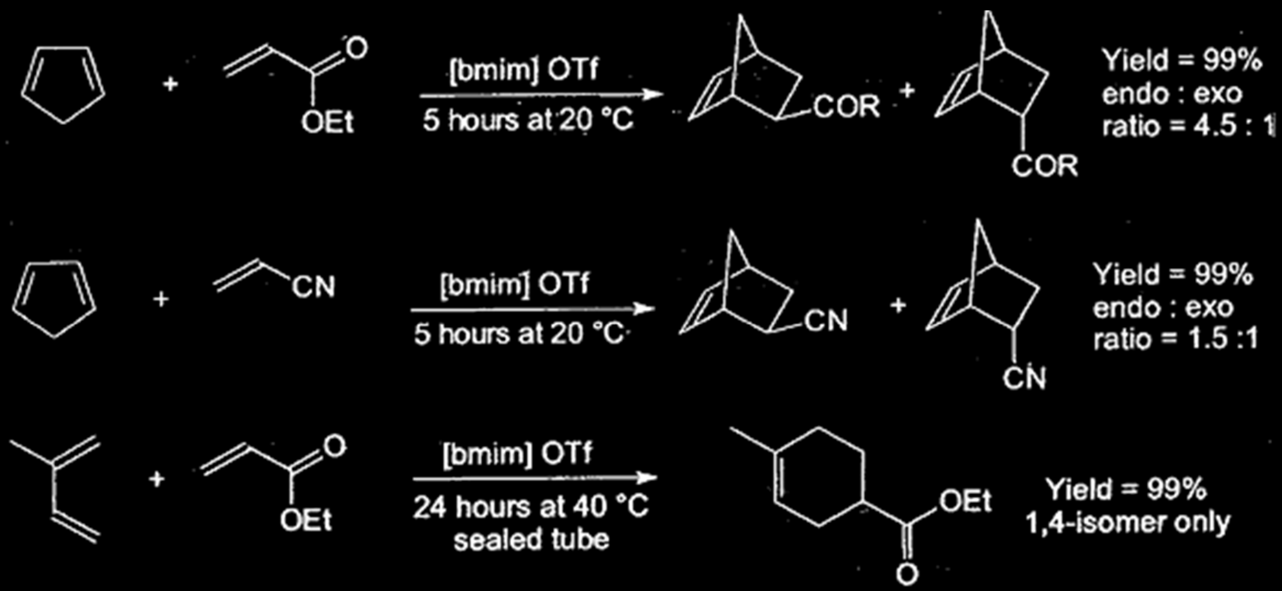


Fig.3. Ionic Liquids permit high yields and selectivity for the Diels-Alder reaction

Effects of Ions

- Effect of cations and anions on the ILs properties.
  - Solubilities and Interaction of super critical CO_2 with anions

Table 1. Ionic liquid-CO_2 solubility(X_{CO2}) and liquid molar volumes(mL/mol) at 40, 50 and 60°C and elevated pressures (Blanchard et al., 2001)

Ionic Liquid	T = 40°C			T = 50°C			T=60°C		
	P(bar)	X_{CO2}	mL/ mol	P(bar)	X_{CO2}	mL/ mol	P(bar)	X_{CO2}	mL/ mol
[bmin][PF_6]	95.67	0.729	71.2	92.46	0.675	83.9	93.01	0.667	84.5
[C_8min][PF_6]	92.67	0.755	80.2	92.67	0.705	103.0	92.88	0.726	94.8
[bmin][NO_3]	92.00	0.513	99.2	92.62	0.530	95.0	93.17	0.522	95.9
[C_8min][BF_4]	92.90	0.708	96.9	92.28	0.671	106.1	93.73	0.651	111.5
[N-bupy][BF_4]	91.59	0.579	94.0	92.35	0.581	92.2	95.80	0.549	98.1
[emim][$EtSO_4$]	92.68	0.423	121.0	94.27	0.403	124.6	94.61	0.457	111.1

Effects of Ions

- Liquid-Liquid Equilibria (Anthony et al., 2001)
  - The mutual solubilites of water and [C_8min][PF_6] are lower than those for the equivalent IL with a short alkyl chain, [bmin][PF_6]
  - Changing the anion from [PF_6] to [BF_4] increases the mutual solubilities.

Table 2. LLE Results for water with Ionic liquids at ambient conditions

	IL in aqueous phase		Water in IL phase	
Ionic Liquid	wt. %	Mol fraction	wt. %	Mol fraction
[C_8min][PF_6]	0.7±0.1	3.5×10^{-4}	1.3 ±0.5	0.20
[bmin][PF_6]	2.0±0.3	1.29×10^{-3}	2.3 ±0.2	0.26
[C_8min][BF_4]	1.8±0.5	1.17×10^{-3}	10.8 ±0.5	0.63

Effects of Ions

- CO_2 Capture by a Task-Specific Ionic Liquid (Eleanor et al. 2001)
  - Interaction between gases and liquid based on separation process
    - Large-scale CO_2 capture is aqueous amines to form ammonium carbamate => loss of capture agent
    - Change the functional group of ionic liquid

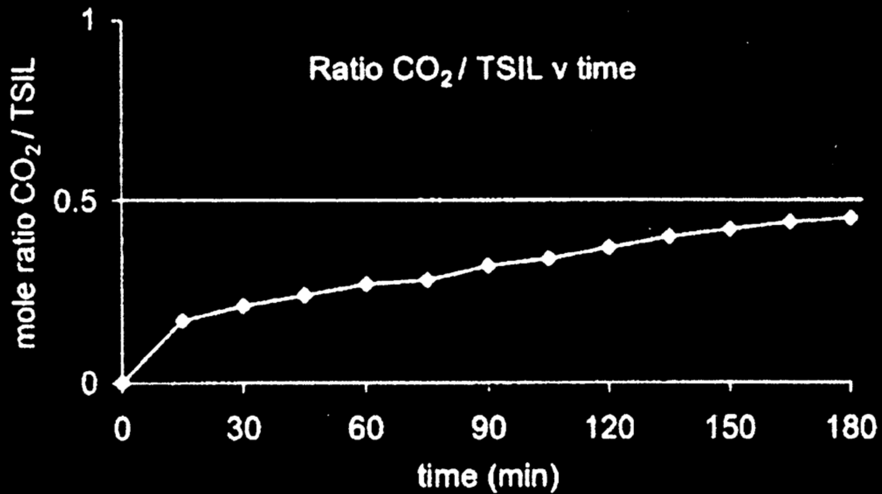


Fig. 4. CO_2/TSIL molar ratio as a function of time

Separation of CO2 from gas mixture

- Strong interaction with Ionic Liquid & CO_2
  - Phase behavior of ILs and pure gases (Jennifer et al. 2002)
    - Ionic liquid : [bmim][PF_6]
    - Carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen
    - Gases that are less soluble in the IL are less soluble in the other solvents
    - However, carbon dioxide is more soluble in the IL than the other solvents
  - The factor to influence the solubility
    - Large dipole moment has high solubility
    - Chemical interaction anion and CO_2
    - Due to large quadrapole monent

Separation of CO_2 from gas mixture

- ILs used by absorber and Supported-liquid Membrane
  - IL can be high selective solvents
    - Used in conventional absorbers
  - Supported-liquid Membrane
    - Limitation
      - conventional liquid slowly evaporate
      - minimum thickness
      - unstable and replenish the solvents

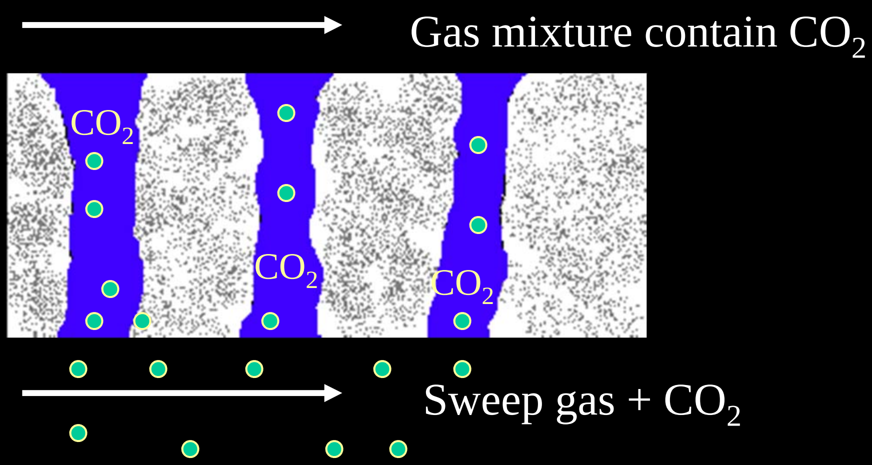


Fig.5. Supported-liquid membrane

Experimental

- Preparation of ILs
  - 1-hexyl-3-methyl-imidazolium tetrafluoroborate
  - 1-ethyl-3-methyl-imidazolium tetrafluoroborate
    - Investigation of alkyl chain length on cation
  - Certification
    - Assay : more than 99%
    - Water contents : less than 1.0%
  - To leave ILs in the vacuum oven at 55 ºC for a week
    - To eliminate water and other gases

Experimental apparatus

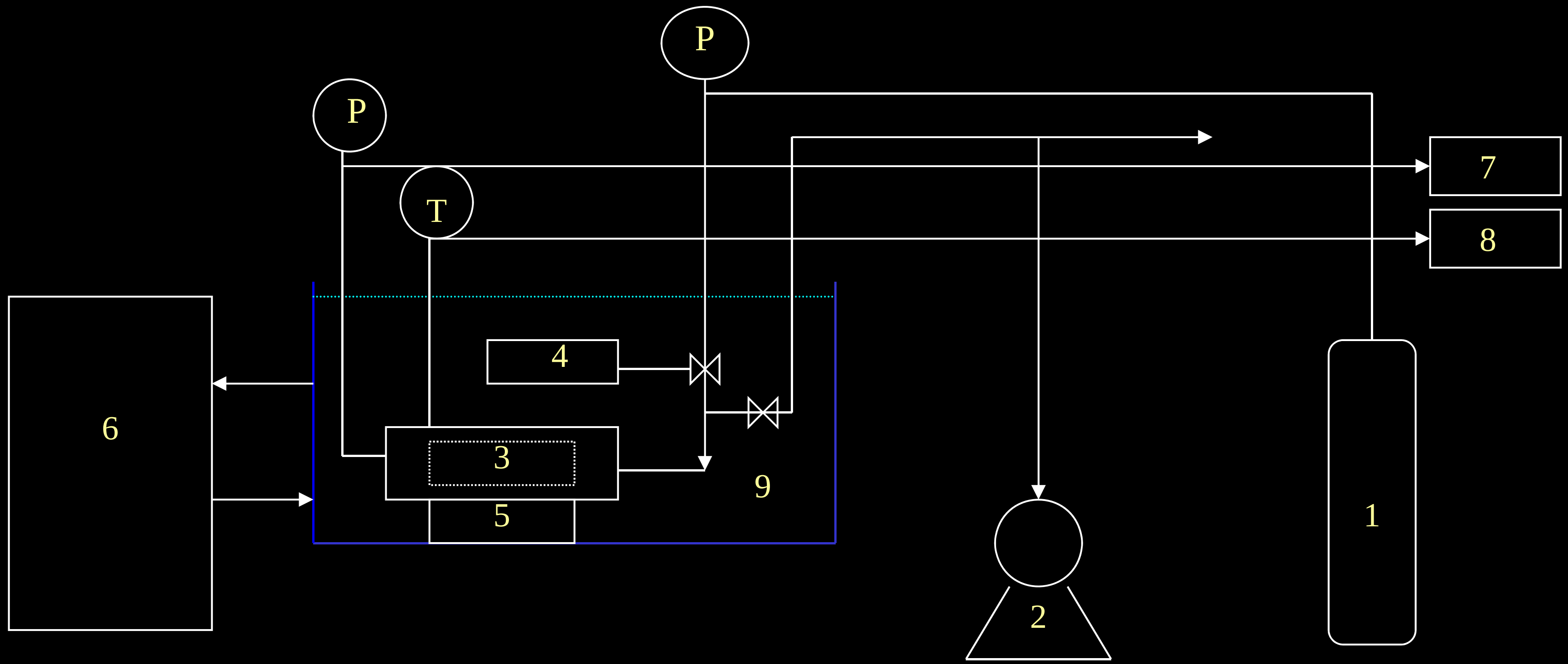


Fig. 6. The experimental apparatus for measurement of the solubility of pure CO_2 gas in the Ionic Liquids

(1) gas bomb ; (2) vacuum pump; (3) view cell (4)small cell (5)magnetic stirrer (6) constant T. circulator (7) pressure indicator (8) temperature indicator (9) water bath

Experimental Method

- Measurement of ILs density at difference temperature
  - Using the pycnometer (5 ± 0.005 ml)
  - Temperature range : 15 – 30 ºC
  - To calculate mole ratio and to predict the solubility

- Solubility of Pure CO_2
  - Pressure range : 1 ~ 10 bar
  - Measurement of the change of pressure in the view cell containing ionic liquids and pure CO_2
  - Calculate the density of CO_2

    (Gas property program of University of Idaho)

- Solubility of CO_2 and other gas mixture