Room Temperature Ionic Liquids

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What are ionic liquids?

- Organic salts composed of cations and anions that are liquid at conditions around room temperature

- No effective vapor pressure, thermal stability, wide range of liquid, and large electrochemical window

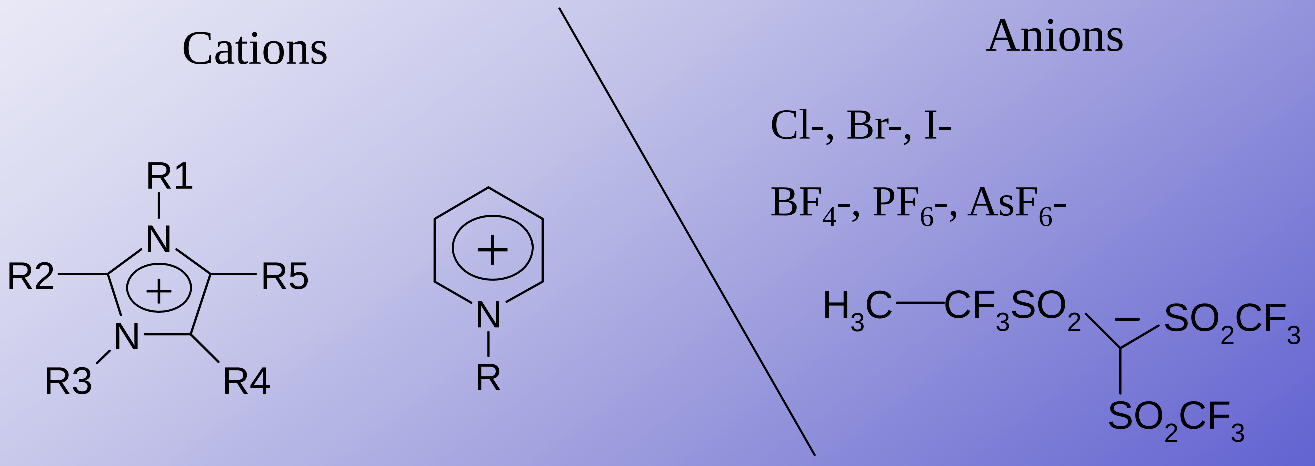

Figure 1. Structure of imidazolium/pyridinium salts

Historical Review

- First discovery of the room temperature ionic liquid
  - N-ethylpyridinium bromide-aluminium chloride melt(Hurley et al., 1951)
- Development of air- and water-stable imidazolium based ILs by Wilkes et al.(1992)
- The range of available anions and cations has expanded enormously in the past decades.
- Application of Chemical synthesis, catalysis, and electrolytes (Holbrey et al., 1999)
- Extraction of organic solutes using ILs and supercritical CO_2 (Blanchard et al., *Nature*, 1999)

Preparation (Hagiwara et al., 2000)

- The reaction of N-alkylimidazole, RIm, with alkyl salts, R’X in appropriate organic solvents
  - $RIm + R'X \longrightarrow RR'Im^{+}X^{-}$

- The anion exchange using N-alkylimidazolium halides
  - Synthesis of alkylimidazolium halides
    - $RIm + R'X' \longrightarrow RR'Im^{+}X'^{-}$ where X’=Cl, Br, I
  - Anion exchange by metathesis of the product with the corresponding acids or their salts
    - $RR'Im^{+}X'^{-} + MX \longrightarrow RR'Im^{+}X^{-} + MX'$

Preparation

- Example :1-Ethyl-3-methylimidazolium tetrafluoroborate (Holbrey et al, 1999)
  - Tetrafluoroboric acid 0.116 mol(48% solution in water 15.2 cm^3) + silver(I) oxide (0.058 mol) in water (50 cm^3)
    - Solution is stirred for a further hour until all the silver(I) oxide completely reacted to give a colorless solution
  - 1-ethyl-3-methylimidazolium bromide(0.116 mol) in water(200 cm^3) was added to the reaction mixture and stirred for 2 hours.
  - Yellow precipitate of silver bromide was removed by filtration and heated at 70°C *in vacuo*.
  - pale yellow liquid, yield 21.36 g (93%)
  - Cost
    - Preparation : about 7,500 won/g
    - Purchasing price (Aldrich) : about 67,000 won/g

Properties of Ionic Liquids

- Melting point (-96°C ~)
  - Melting point is lowered as increasing length of alkyl chain in cations. (Larsen et al., 2000)
    - The increasing disruption of crystal packing overrides increased van der Waals interactions between the larger components.
  - C-2 position of the imidazolium cation : Hydrogen bonding
    - Carborane salts : Methylation of the C-2 position of the imidazolium cations does not lower melting points. (Larsen et al.,2000)
    - Tetrafluoroborate salts : The evidence for hydrogen bonding is inconclusive.(Holbrey et al., 1999)
    - In general methylation of C-2 position increases the melting points.
      - The effect of the van der Waals interaction via methyl group dominates over the electrostatic interaction via proton on C-2.(Hagiwara et al., 2000)

Properties of Ionic Liquids

- Density (Hagiwara et al., 2000)
  - 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.

- Viscosity (Hagiwara et al., 2000)
  - 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.

Properties of Ionic Liquids

- Polarity
  - The simplest indicators of solvent strength
  - Aki et al.(*Chem. Commun.*, 2001)
    - [BMIM][PF_6], [C_8mim][PF_6], [BMIM][NO_3], and [N-bupy][BF_4] are more polar acetonitrile and less polar than methanol.
    - Theses ionic liquids are expected to be at least partially miscible with water
  - Carmichael et al.(*J. Phys. Org. Chem.* 2000)
    - 1-alkyl-3-methylimidazolium ionic liquids
    - Anion : [PF_6], [BF_4], [$(CF_3SO_2)_2N$], and [NO_3]
    - They are in the same polarity region as 2-aminoethanol and lower alcohols (methanol, ethanol and butan-1-ol)

Properties of Ionic Liquids

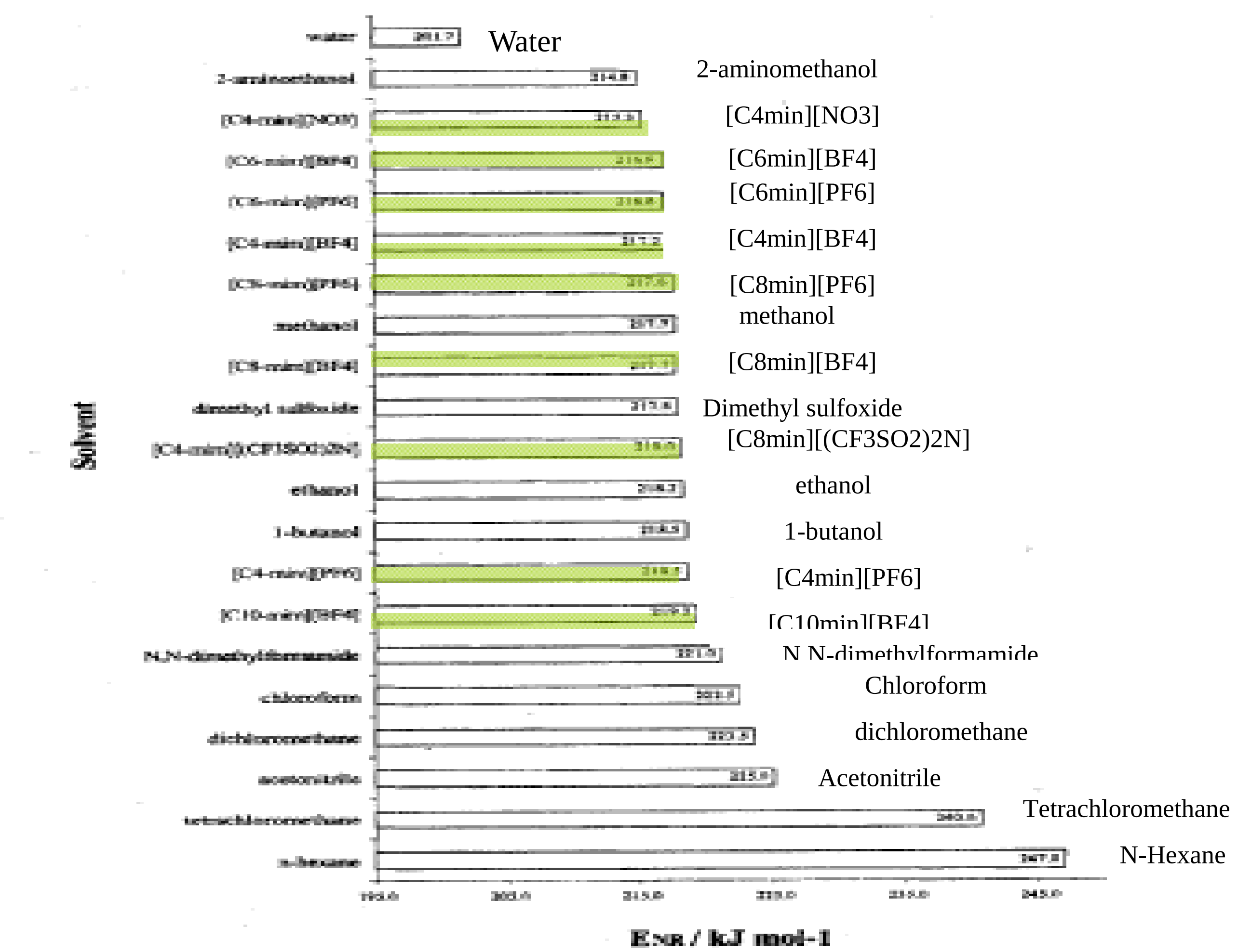

Figure 2. E_{NR} values for $[C_n\text{-min}]X$ ionic liquids and common conventional solvents

Phase Behavior of Ionic Liquid and Water

- The cross contamination of the aqueous and IL rich phases
  - The presence of IL in the aqueous phase : Environmental problem
  - The presence of water in the IL phase can dramatically affect the physical properties

- General guide lines on IL/water miscibility(Seddon et al, 2000)
  - Halide, ethnoate, nitrate and trifluoroacetate salts : totally miscible
  - $[PF_6]$ and $[(CF_3SO_2)_2N]$: immiscible
  - $[BF_4]$ and $[CF_3SO_3]$: totally miscible or immiscible depending on the substituents on the cation

Phase Behavior of Ionic Liquid and Water

- Vapor–Liquid Equilibria (Anthony et al., 2001)
  - Using a gravimetric microbalance(IGA 003, Hiden Analytical)
  - Measuring the weight change of IL phase as water vapor absorb into ionic liquid
  - Water is more soluble in systems where the counteranion is [BF_4] rather than [PF_6]. => higher charge density for [BF_4]
  - Increasing the alkyl chain decreases the solubility of water.

Phase Behavior of Ionic Liquid and Water

- Liquid-Liquid Equilibria (Anthony et al., 2001)
  - IL contents in the water-rich phase : UV-vis spectroscopy
  - Water content in the IL-rich phase : Karl Fisher titrator
  - 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 1. 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

Phase Behavior of Ionic Liquid and Carbon Dioxide (Blanchard et al., 2001)

- Large quantities of CO_2 dissolve in the IL phase, but no appreciable amount of IL solubilize in the CO_2 phase
- The water impurity in the IL is the likely culprit responsible for the low CO_2 solubilities in the water-saturated IL-rich phase.

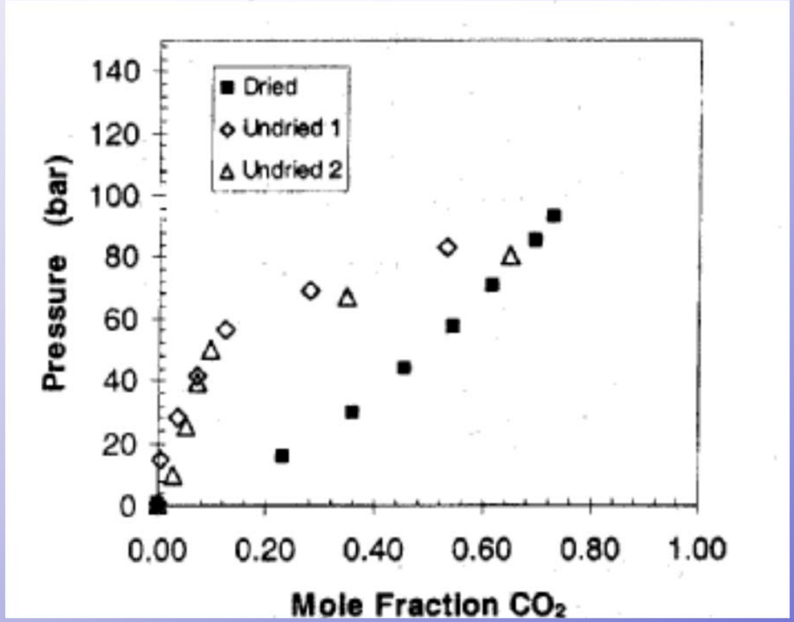

Figure 3. [bmin][PF_6]-CO_2 liquid phase compositions for dried vs. wet ionic liquid samples at 40°C

Phase Behavior of Ionic Liquid and Carbon Dioxide

Table 2. Ionic liquid-CO2 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

Phase Behavior of Ionic Liquid and Carbon Dioxide

- The solubility of CO2 in ILs
  - ◆ The greast solubility in the ILs with the PF_6^- anion.
  - ◆ The slight change with temperature for all of the ILs

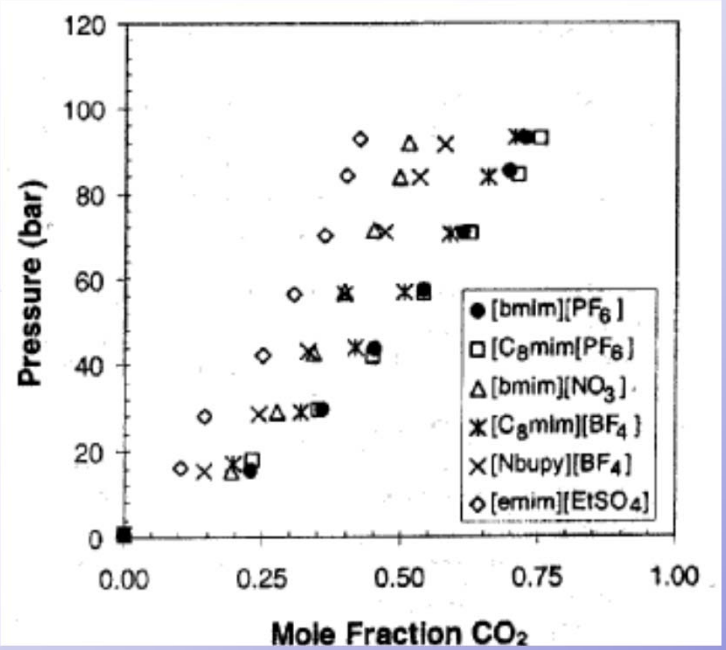

Figure 4. Liquid phase compositions of six ionic liquid-CO2 mixtures at 40°C

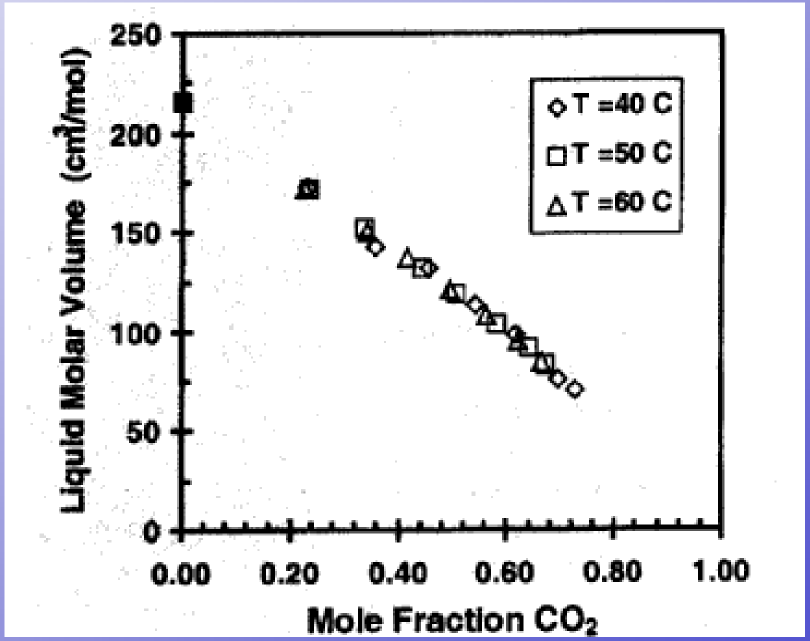

Figure 5. [bmin][PF_6]-CO2 liquid phase compositions at 40, 50, and 60°C

Application (I)

- Recovery of organic products from ionic liquids using supercritical carbon dioxide(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.

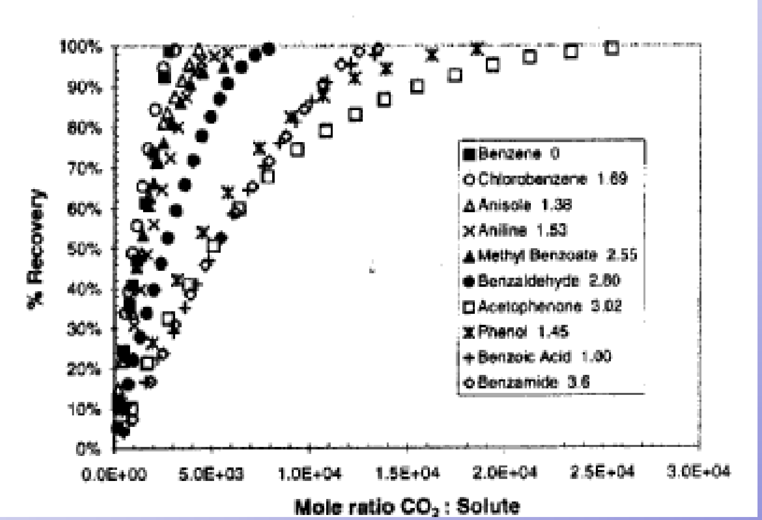

Figure 6. Extraction of aromatic solutes from [bmim][PF_6] with $SCCO_2$ at 40 °C and 138 bar

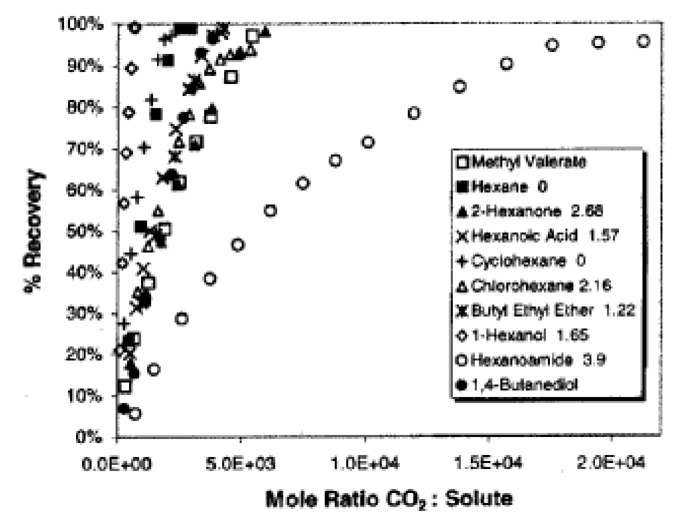

Figure 7. Extraction of aliphatic solutes from [bmim][PF_6] with $SCCO_2$ at 40 °C and 138 bar

Application (II)

- Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids(Dai et al., J.Chem.Soc.,Dalton Trans., 1999)
  - Improving the ability of crown ethers to remove metal ions from aqueous solutions
  - The highst distribution coefficient value is over four orders of magnitude greater than those of the conventional extraction systems.

Extract phase	D(with crown ether)	D(without crown ether)
BuMe2ImPF6	**4.2**	**0.67**
BuMeImPF6	**2.4×10^{1}**	**0.89**
EtMe2ImTf2N	**4.5×10^{3}**	**0.81**
EtMeIMTf2N	**1.1×10^{4}**	**0.64**
PrMe2ImTf2N	**1.8×10^{3}**	**0.47**
PrMeImTf2N	**5.4×10^{3}**	**0.35**
Toluene	**7.6×10^{-1}**	**Not measurable**
Chloroform	**7.7×10^{-1}**	**Not measurable**

References

- Aki, S.N.V.K., Brennecke, J.F. and Samanta, A., *Chem. Commun.*, **2001**, 413
- Anthony, J.L., Maginn, E.J. and Brennecke, J.F., *J. Phys. Chem. B*, **2001**, 105, 10942
- Blanchard, L.A., Hancu, D., Beckman, E.J. and Brennecke, J.F., *Nature*, **1999**, 399, 28
- Blanchard, L.A., Gu, Z. and Brennecke, J.F., *J. Phys. Chem. B*, **2001**, 105, 2437
- Blanchard, L.A. and Brennecke, J.F., Ind. Eng. Chem. Res., 2221, 40, 287
- Carmichael, A.J. and Seddon, K.R., *J. Phys. Org. Chem.*, **2000**, 13, 591
- Dai, Sheng, Ju, Y.H., and Barnes, C.E., *J. Chem. Soc., Dalton Trans.*, **1999**, 1201
- Hurley, F.H. and Wier, T.P., *J. Electrochem. Soc.* **1951**,98,203
- Holbrey, J.D. and Seddon, K.R., *Clean Prod. Process*. **1992**, 13, 965
- Hagiwara, R. and Ito, Y., ***J. Fluor. Chem***. **2000**, 105, 221
- Holbrey, J.D. and Seddon, K.R., *J. Chem. Soc., Dalton Trans.*, **1999**, 2133
- Larsen, A.S., Holbrey, J.D., Tham, F.S. and Reed, C.A., *J. Am. Chem. Soc.*, **2000**, 122, 7264
- Seddon, K.R., Stark, A. and Torres, M.J., *Pure Appl. Chem*. **2000**, 72, 2275
- Wilkes J.S. and Zaworotko, M.J., *J. Chem. Soc. Chem. Commun*. **1992**, 965