Room-Temperature Ionic Liquids for Separations Processes?

Micelle formation in ionic liquids

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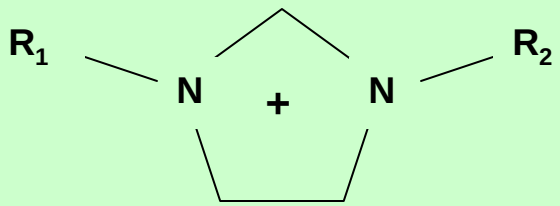
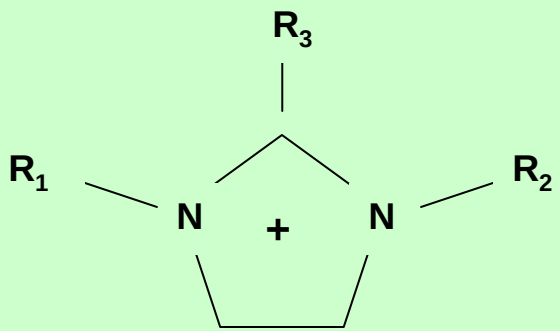
Structures of IL used



where: $R_1 = CH_3$
$R_2 = (CH_2)_{n-1}CH_3$
1-C_n-3-methylimidazolium ($C_n$mim$^+$) cation



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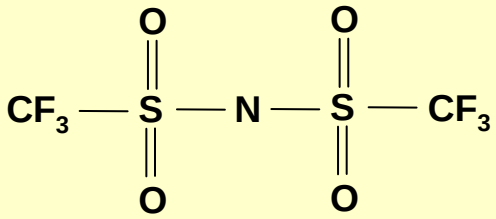
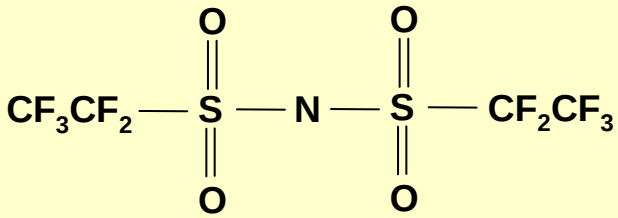
Hydrophobic Anion



bis(trifluoromethanesulfonyl) imide (Tf_2N) anion



bis(perfluoroethylsulfonyl) imide (BETI) anion

Water-Soluble Anion

Bromide Anion

Overview

1. **RTIL for Separations Processes?**
   A. **Solubility Measurements**
      - Hydrophobic RTILs in Aqueous Solutions
      - Effects of Salts (NaCL and KCL)
      - Water-Soluble IL in Water
   B. **Electrostatic Spraying of RTIL**
      - Surface Tension and Electrical Conductivity of Water in L-L-E with RTIL
      - Three RTIL-in-immiscible solvent systems were investigated
        - [C4mim]Tf2N-in-Water system
        - [C6mim]BETI-in-Water system
        - [C4mim]Tf2N-in-Octane system

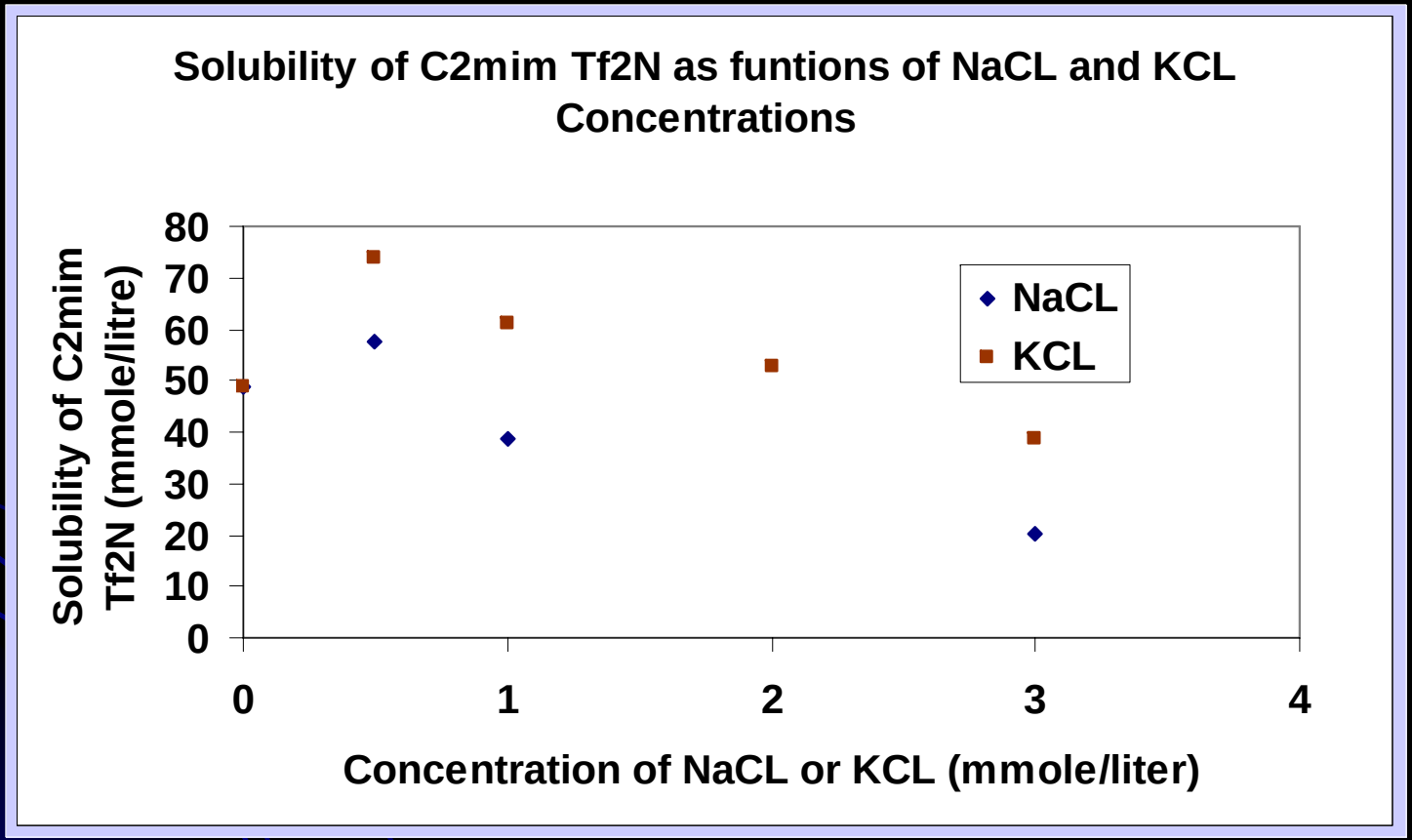
Overview

2. **Micelle Formation in IL**
   A. **Surface Tension and Electrical Conductivity Measurements of Water-Soluble IL**
      - To determine the critical micelle concentration (CMC) of the ionic liquids
   B. **Dynamic Light Scattering and Small Angle X-ray Scattering**
      - To obtain a microscopic view of the behavior of ionic liquids in solution

1A: Solubility of Hydrophobic RTILs in Aqueous Solutions at room temperature and pressure

	Tf2N				BETI			
	C_2mim	C_4mim	C_6mim	C_8mim	C_2mim	C_4mim	C_6mim	C_8mim
Water (mM)	48.9	15.7	7.24	4.08	9.22	4.46	1.39	0.388
1M NaCL (mM)	38.5	12.9	4.32	1.41	7.38	2.71	0.966	0.284
3M NaCL (mM)	20.3	6.51	3.05	0.702	2.87	0.980	0.298	0.097

1A: Effects of Salts (NaCL and KCL) on the RTIL solubility in Aqueous Solution



Discussions:

- Solubility of hydrophobic RTILs in aqueous solutions depends significantly on both the cation and anion
  - The longer the alkyl chain length, the more hydrophobic the RTIL
  - The additional C2F4 on BETI makes the BETI IL more hydrophobic than the Tf2N IL
- RTILs solubility in water is sensitive to the presence of non-complexing electrolyte salts
  - The initial increase in solubility is due to the increase in solubility product with the presence of additional ions in solution
  - The eventually decrease in solubility is due to the salting-out effect when the hydrophobic RTILs precipitates out of the aqueous solution

1A: Solubility of solid phase water-soluble imidazolium-based ILs in aqueous solution at room temperature and pressure (weight % in water)

C_{12}mim	C_{14}mim	C_{16}mim	C_{12}bmim	C_{14}bmim	C_{16}bmim
95<x<106	>58	0.27	>104	>68	25<x<53

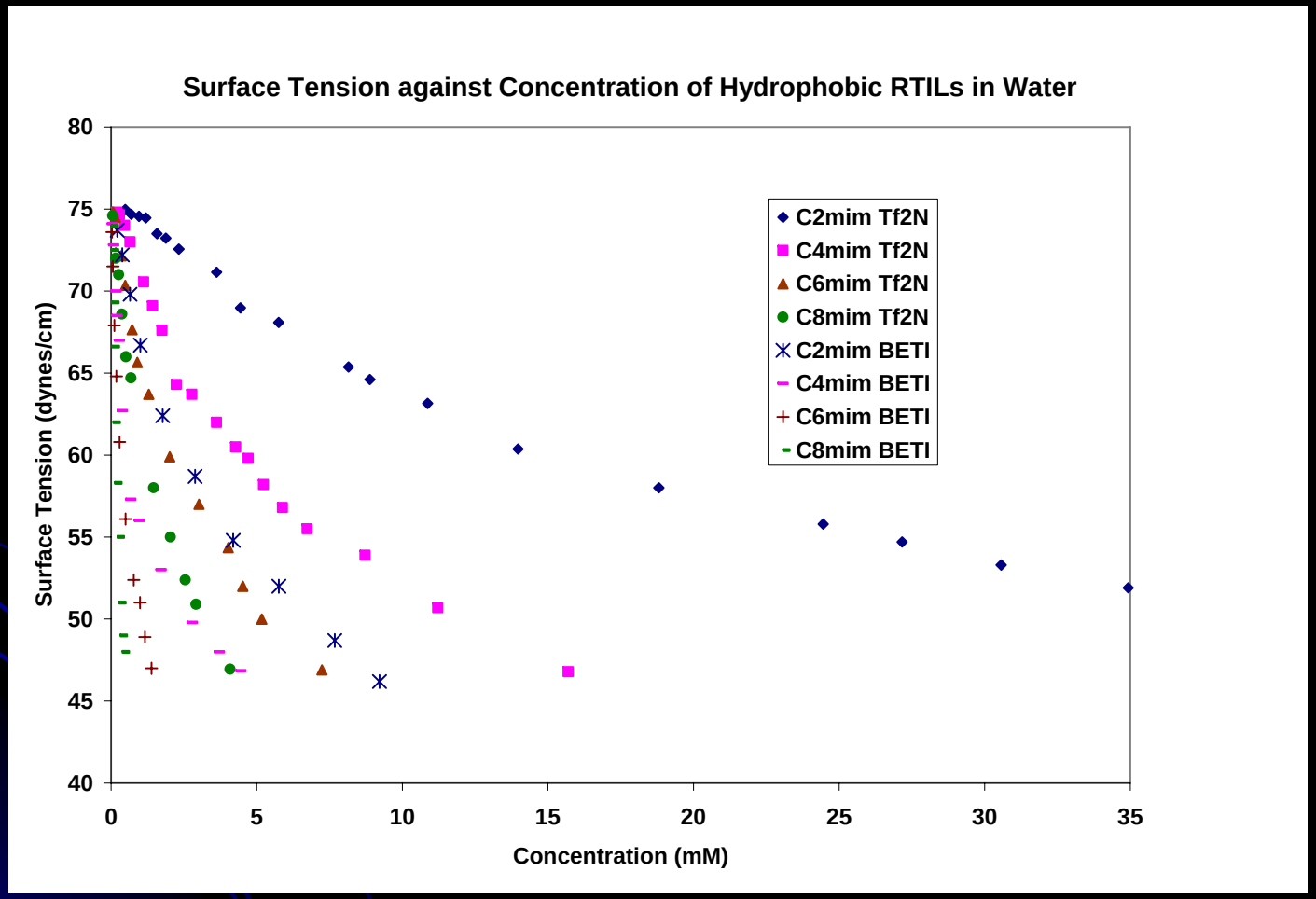
Discussions:

- C16bmim Bromide >25 weight % in water
- C16mim Bromide 0.27 weight % in water
- C14mim Bromide >58 weight % in water

- Additional methyl group on the aromatic ring of the RTIL significantly increase its solubility in aqueous solution

- Solubility of IL in water decreases as the alkyl chain length increases

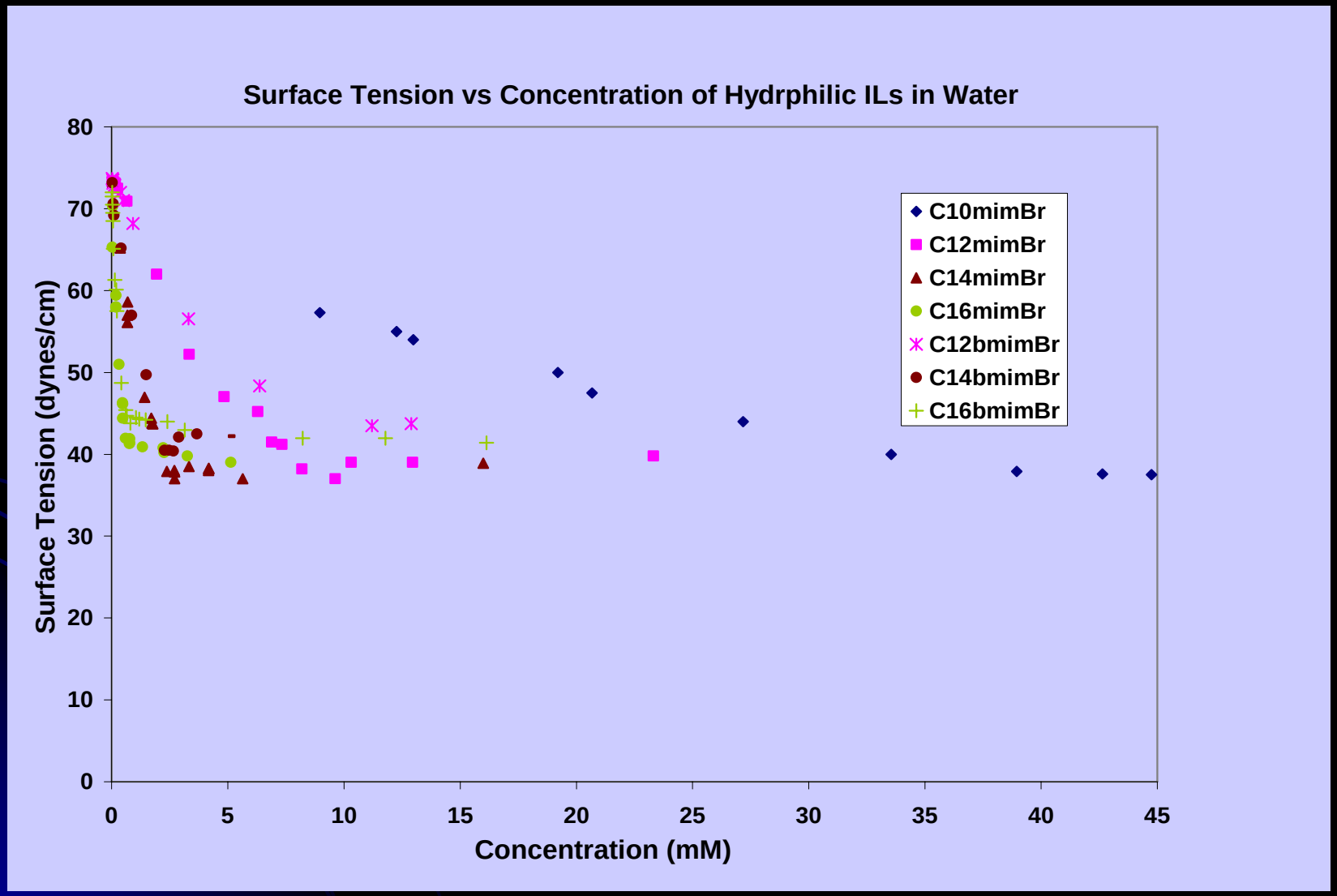
1B: Surface Tension and Electrical Conductivity of Water in L-L-E with RTIL



Discussions: Surface Tension

- **For the same RTIL concentration, the most hydrophobic RTIL has the most significant reduction in the surface tension of the aqueous solution**
  - The more hydrophobic ionic liquids prefer to accumulate at the air/water interface than in the bulk solution, resulting in a greater decrease in the surface tension for the same RTIL concentration

Surface Tension Measurements of the Water-soluble ILs



Discussions: Surface Tension Measurements of the Water-soluble ILs

- **As the surface tension of the aqueous phase of the water-soluble ILs reached 39dynes/cm, addition of more IL into the aqueous phase no longer reduces the surface tension**
  - Reinforce the model of having concentration gradients in the aqueous phase; where even the water-soluble IL prefers to accumulate at the air/water interface.
  - Addition of more IL eventually leads to a saturation concentration of the ILs at the air/water interface.
  - After that, additional IL only goes into the bulk solution, thus the surface tension of the aqueous solution remain unchanged.

1B: Electrical Conductivity of Water in L-L-E with RTIL

	Tf2N				BETI			
	C2	C4	C6	C8	C2	C4	C6	C8
Electrical Conductivity (microS/cm)	2350	735	283	178	518	193	60.4	20.3

Electrical conductivity measurements of de-ionized water at liquid-liquid equilibrium with the hydrophobic imidazolium-based RTILs, where electrical conductivity of de-ionized water is 1.1 microS/cm

Electrostatic Spraying

Behavior of [C4mim][Tf2N] for a number of potentials at the nozzle tip during the electrostatic spraying of [C4mim][Tf2N] into octane.

[a] Voltage = 0 V

Dripping mode

[b] Voltage = 2 kV

Dripping mode
Dripping frequency increases and drop diameter decreases

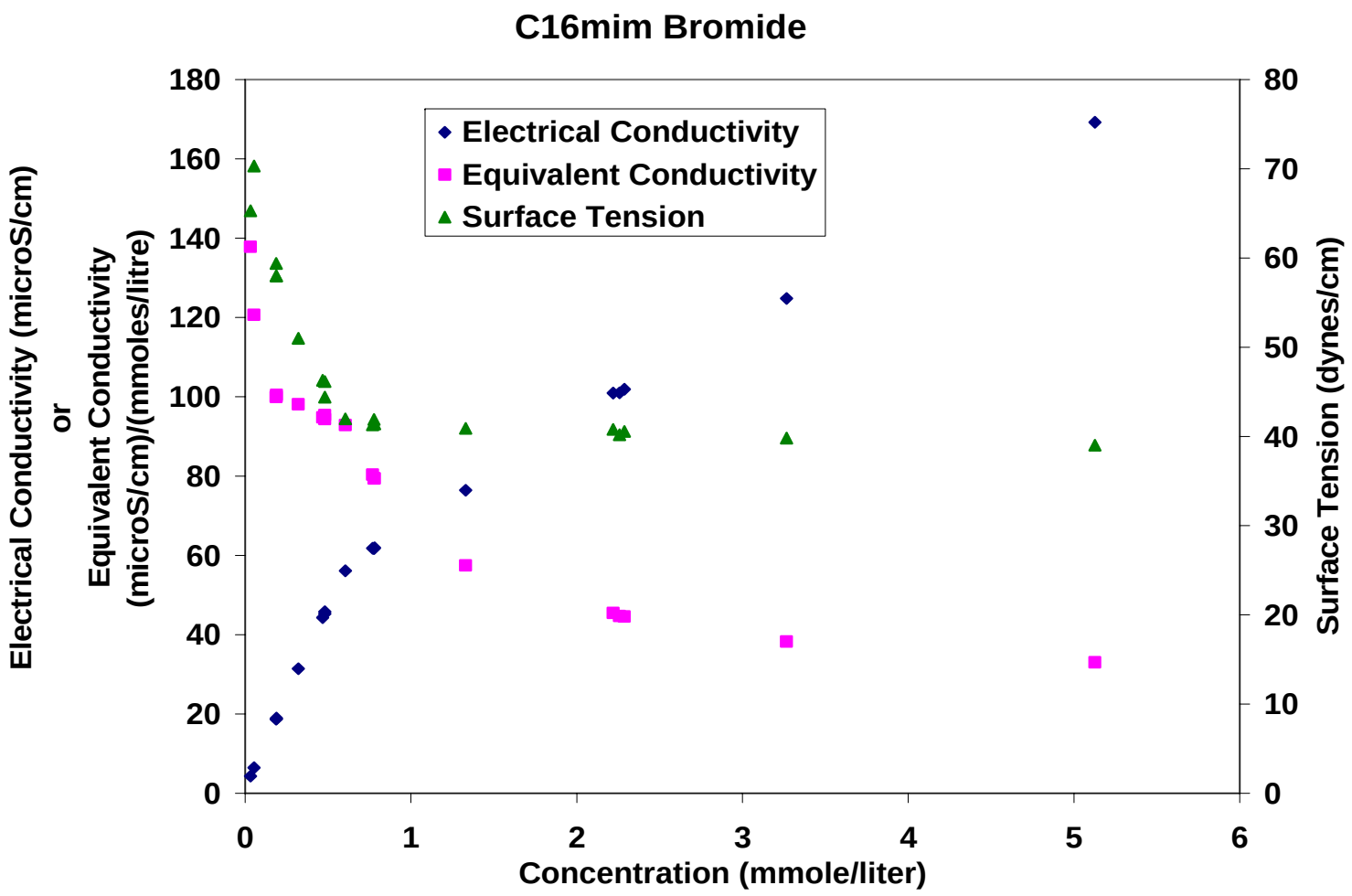
[c] Voltage = 5 kV

Stable jet mode

Discussions:

- RTILs reduces the surface tension of the aqueous phase significantly, making it easier for the RTIL to form emulsions
- However, these immiscible RTILs made the surrounding water phase conductive, causing undesirable sparking and a jump in the electric current.
- Hence, of the 3 immiscible fluids systems studied for electrostatic spraying, only the system with octane as the continuous phase worked well.
- Electrostatic spraying of these immiscible RTILs into de-ionized water may work for a co-current flow.

2A: Determination of CMC from Electrical Conductivity and Surface Tension Measurements



2A: CMC values (mmole/litre) of the water-soluble bromide ionic liquids obtained from surface tension and conductivity measurements

Anion	Cation	Surface Tension	Electrical Conductivity	Equivalent Conductivity
Bromide	C_{16}bmim	0.6	0.7	0.7
	C_{14}bmim	2.3	2.3	2.3
	C_{12}bmim	9.5	10	10
	C_{16}mim	0.6	0.6	0.6
	C_{14}mim	2.3	2.5	2.5
	C_{12}mim	10.5	11	11
	C_{10}mim	41	42	42
	C_{9}mim	73	78	78

Discussions:

- As the alkyl chain length increases, the CMC of the ionic liquids decreases.
- The additional methyl group on the aromatic ring of the cation does not appear to have a significant effect on the CMC of the ionic liquid.

Dynamic Light Scattering

De-ionized Water sample

Run Number	1	2	3	4	5
Effective Diameter (nm):	0.6	0.5		0.4	0.6
Diameter (nm):	1.3	0.9		1.5	1.6
poly. dispersion:	0.1522	0.1417		0.1482	0.1818

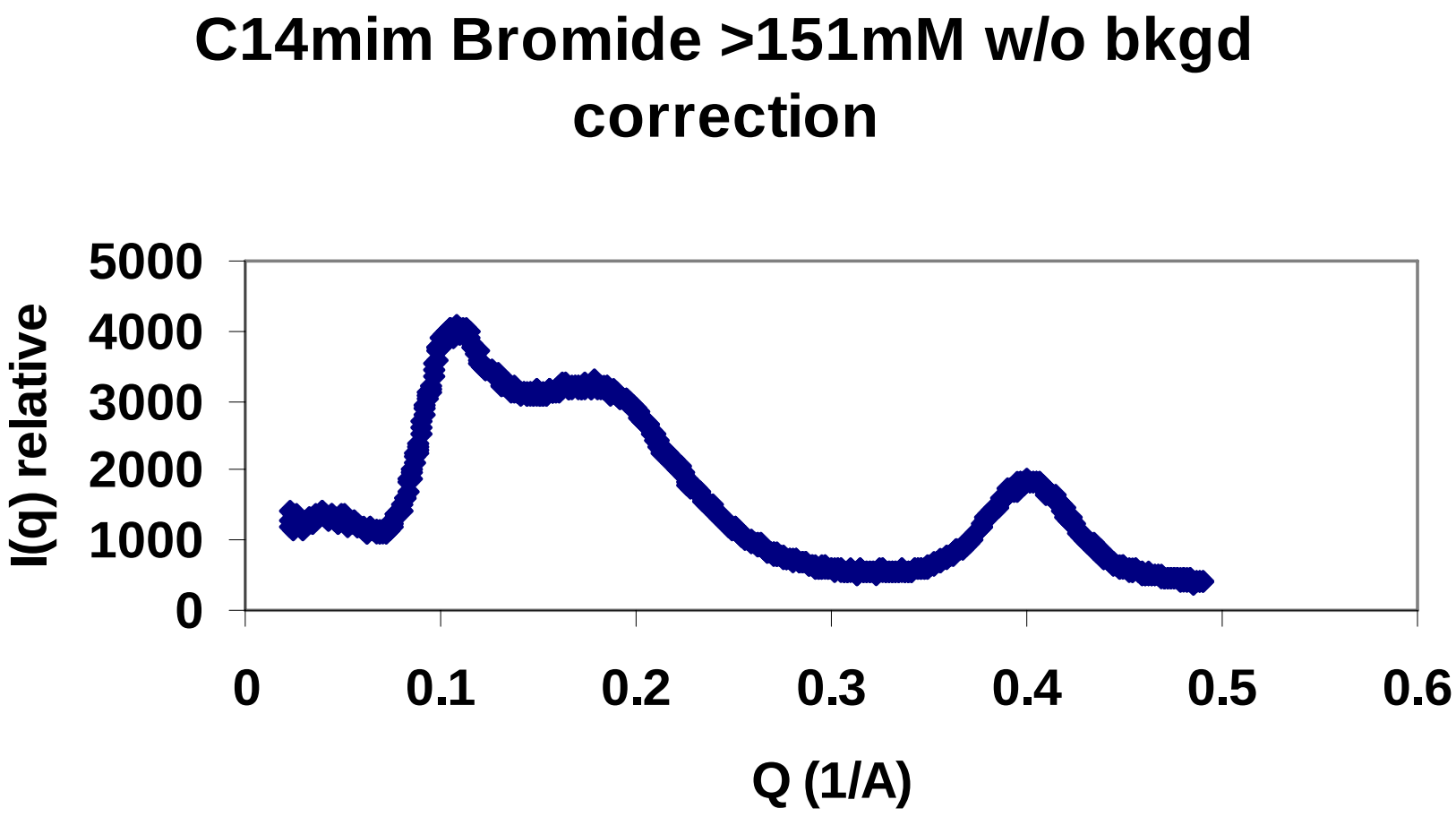
C14mim Bromide > 151mmole/litre

Run Number	1	2	3	4	5
Effective Diameter (nm):	0.9	2.9	1.1	2.6	1.1
Diameter (nm):	2.4	6.5	3	9.1	3.1
poly. dispersion:	0.1621	0.2152	0.1767	0.2044	0.2093

Discussion:

- Comparison between data obtained from DI water sample and C14mim Bromide ionic liquid aqueous solution sample showed that the diameter of the particles detected in the ionic liquid sample was constantly larger than those detected in the DI water phase.

Small Angle X-Ray Scattering



Discussions:

- The first and the last peak observed correspond to the peak by the kapton windows. There were two other peaks detected which correspond to the particles in solution of C14mim Bromide aqueous solution, not found in DI water sample.

Summary of main findings

- Significant solubility of hydrophobic ionic liquids were measured
- Aqueous solubility of hydrophobic ionic liquids decreases as the length of the alkyl chain length on the cation increases
- Aqueous solubility of hydrophobic ionic liquids is sensitive to the presence of non-complexing electrolyte salts (NaCL and KCL)
- Ionic liquids have surface active properties in aqueous solution – allowing electrostatic spraying of ionic liquid into another immiscible solvent for efficiently generating interfacial area
- However, the applicability of electrostatic spraying of ionic liquids is limited by the increase in the electrical conductivity of the surrounding aqueous phase due to the dissolution of the ionic liquid
- The variation of surface tension and conductivity measurements with concentration of ionic liquids revealed breakpoint that is indicative of aggregation of long alkyl chain length of C9 and longer cations ionic liquids in solution
- Experimental results from dynamic light scattering and SAXS showed the presence of particles in C14mim Bromide ionic liquids aqueous solution sample with concentration greater than 151mmole/litre, that are not found in de-ionized water sample.
- The above information will be important in determining the feasibility of using ionic liquid for industrial processing.

Acknowledgements

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