Multifunctional Ionic Liquids and their use in the formation of co-ordinated structures

Andrew Kavanagh, Robert Byrne, Dermot Diamond, Aleksandar Radu
CLARITY, The Centre for Sensor Web Technologies,National Centre for Sensor Research,
School of Chemical Sciences,Dublin City University,Ireland.

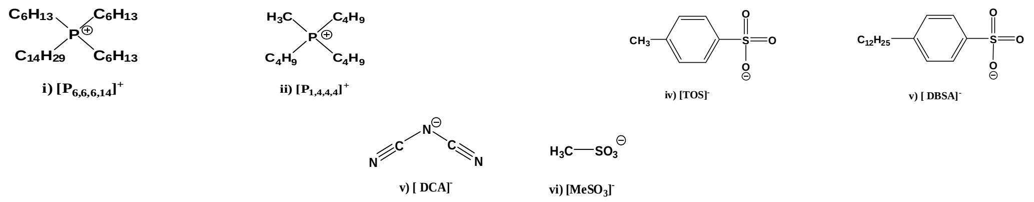

Fig 1 : The Ionic Liquids used in this study; i) trihexyltetradecylphosphonium, ii) methyltriisobutyl phosphonium, iii) toluene sulfonate, iv) dodecylbenzene sulfonate, v) dicyanamide and vi) methane sulfonate.

INTRODUCTION:

We have studied the IL $[P_{6,6,6,14}][DCA]$ as a *self-indicating, simultaneous, multianalyte recognition system* for heavy metal ions such as Cu^{2+} and Co^{2+}. When incorporated into a polymer membrane, this system maintains all these attractive features with the added bonus of the IL now being *self-plasticizing*.

Other anions mentioned are considered to be "soft" or non-coordinating[1]. We have used heat to change the chemistry of these anions, resulting in ion coordination to previously solvating molecules. These solvating anions have in common a sulfonate moiety that can co-ordinate to a given heavy metal.[2] The formation of these structures has been characterized via UV/Vis and Infrared Spectroscopy.

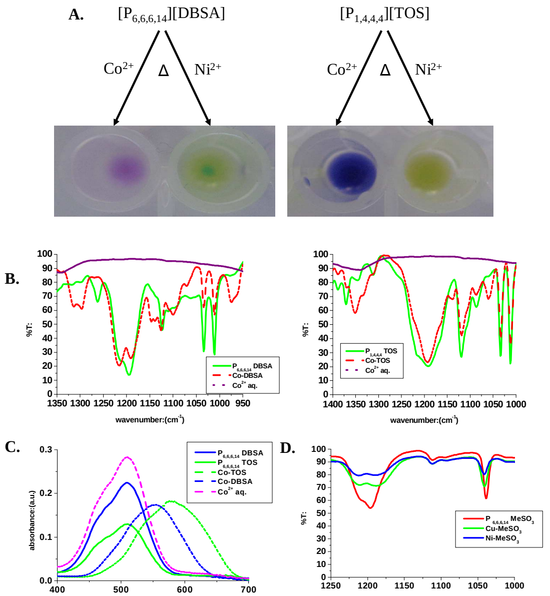

Fig 3:
A) The various colours seen upon thermal activation of IL's containg $[DBSA]^-$ and $[TOS]^-$
B) IR spectra obtained for the thermal complexation of i) Co^{2+} to the $[DBSA]^-$ anion and ii) Ni^{2+} to the $[TOS]^-$ anion.
The most striking difference appeared at 1200cm^{-1}, which we attributed to one of the contributions of the SO_3 group.
C) UV/Vis absorption spectra obtained before and after thermal activation of anions
D) IR spectrum obtained for phosphonium IL containing methane sulfonate, which co-ordinates to heavy metals through its sulfonate group. We observed similar IR features at 1200cm^{-1}.

CONCLUSION:

Due to their inherent natural composition, these Ionic liquids have proven to be a good media in which to study co-ordination chemistry.
We have demonstrated firstly the multifunctional co-ordination chemistry of the anion $[DCA]^-$ used in modern day Ionic Liquids. Adding to this multifunctionality is the plasticizing feature of this system, attributed to the large phosphonium cation.
We have also demonstrated the interesting effects of heat on the chemistry of other widely used Ionic Liquids, with possibly some new structures formed.

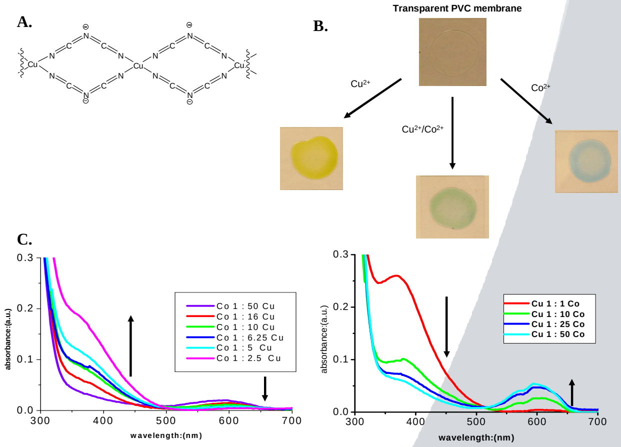

Fig 2: A) One of the many possible co-ordinated structures of dicyanamide (DCA)
B) As opposed to a colourless IL based membrane, a complex metal ion-[DCA] membrane is highly coloured, enabling optical detection, eliminating the need for a responsive chromophore.
C) Multianalyte recognition based on two distinct absorption maxima;
By keeping the concentration of Co^{2+} constant, and incrementally increasing the amount of Cu^{2+} (left hand side), we have noted an inverse relationship in the absorption maxima.
We also noted the same inverse relationship when doing the mirror experiment (right hand side).

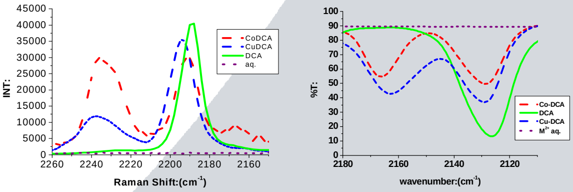

Fig 4: Vibrational spectra obtained for the complexation of $Co^{2+}$and Cu^{2+} to $[DCA]^-$. The primary binding mode of the ligand appears to be end to end bridging through both terminal cyanide Nitrogen atoms.

Highlighted above are the cyanide stretches observed in both i) Raman and ii) Infrared Spectroscopy. Upon complexation a new stretch is formed in this region, this new stretch is a function of the electronegativity of the metal[2].

REFERENCES:

1. MacFarlane et al; *ChemComm*, 1905-1917; **2006**
2. Nakamoto, K; *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 5th Edition ed.; Wiley: New York, **1997**

ACKNOWLEDGEMENT:

This work was supported by DCU Research Career Start Fellowship 2008, Enterprise Ireland (grant 07/RFP/MASF812) and Science Foundation Ireland (grant 07/CE/I1147).

This work is supported by Science Foundation Ireland under grant 07/CE/I1147

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