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Title:

The inherent physical, optical and conductivity properties of Ionic Liquid – polymeric membranes; a self indicating, simultaneous response upon coordination to transitional metal ions.

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Ionic Liquids (IL's) are organic salts that are liquid at room temperature. Typically, they contain a bulky, asymmetric organic cation and a small inorganic/organic anion held together via weak electrostatic interactions, which prevents them from forming a structured lattice.
They exhibit many favourable physical and chemical characteristics, which has led to their use in a variety of analytical techniques [1]. All IL's display a measured ionic conductivity, plus liquid properties such as density and viscosity can be controlled by correct choice and/or chemical functionalisation of the ion pair [2].
Ion Selective Electrodes (ISE's) utilise polymeric membranes for the detection of a target ion in trace amounts. They typically require a polymer and plasticizer, plus also an ion-exchanging salt and an ionophore which will selectively bind to a target ion [3]. The response of a target ion binding to an ionophore can be monitored electrochemically, or optically if the ion-ionophore complex produces a colour.
There are several reports in which IL's plasticize both *polyvinylchloride* (PVC) and *polymethylmethacrylate* (PMMA) based membranes for use in ISE's [4]. Furthermore IL's also act as ion-exchangers, thereby eliminating the need for facilitated transport of target ions from aqueous to organic phase.
We will describe the work done to date on the IL *trihexyltetradecylphosphonium dicyanamide* $[P_{6,6,6,14}][DCA]$ and its use in polymeric membranes typical of ISE's. Once solidified into a PVC membrane, $[P_{6,6,6,14}][DCA]$ can not only act as the plasticizer and ion-exchanger, but also as the ionophore, producing a colorimetric response upon coordination to Cu^{2+} (yellow), Co^{2+} (blue), but also both ions *simultaneously* (green).
The multifunctionality of $[P_{6,6,6,14}][DCA]$ leads to a dramatic simplification of membrane components, producing a system capable of a self-indicating, simultaneous, colorimetric response.
As well as a selective optical response, we have also explored the possibility to see if the inherent conducting properties of these membranes can be exploited. Radio frequency (RF) detection provides a technique which can monitor the conductivity of a sample wirelessly, but also has the required sensitivity and is non-invasive on the sample.
RF can not only discriminate between the coordinated and non-coordinated membranes, but also between the individual co-ordinated membranes. The resultant downward trend in conductivity from *Blank > Cobalt > Mixture > Copper* has been validated by Electrochemical Impedance Spectroscopy (EIS) and by portable X-Ray Fluorescence (XRF).
XRF shows that the results obtained from RF and EIS are directly related to the binding selectivity of the ligand $[DCA]^-$. We have observed the highest binding levels for membranes exposed to Cu^{2+} ions, thereby producing the lowest RF conductivity signal and the highest impedance values. The opposite applies for Co^{2+}, we have observed lower binding values, conversely producing the highest co-ordinated RF signal and the lowest coordinated impedance values.
IL's have been shown to bind to a variety of heavy metal ions [5], lanthanide ions[6] plus important target analytes such as CO_2 [7]. If a change in conductivity can be presumed upon binding to the analyte, then the inherent conductivity of IL's could be exploited in future electrochemical sensing.

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