

A Two-Component Polymeric Optode Membrane based on a Multifunctional Ionic Liquid

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2.1 Abstract

This work details the use of a 2-component optode membrane which is capable of generating three distinct colours in the presence of Cu^{2+} and Co^{2+} ions. It has been found that the ionic liquid (IL) *trihexyltetradecylphosphonium dicyanamide* [$P_{6,6,6,14}$][DCA] can act as plasticizer, ligand and transducer dye when used in *poly(vinylchloride)* (PVC) membranes, which significantly simplifies the optode membrane platform. Upon exposure to an aqueous Cu^{2+} solution, a yellow colour is generated within the membrane, while exposure to aqueous Co^{2+} solution generates a blue colour. Exposure to a solution containing both ions produces a green colour. Vibrational spectroscopy has been used to investigate molecular basis of the IL-metal binding mechanism. Analytical characteristics of the membranes including the effect of interfering ions, binding constants and the limit of detection for both ions have been estimated. Finally the case of simultaneous dual-analyte recognition is presented based on two distinct absorption maxima.

2.2 Introduction

The vast majority of chemical sensors are based on a ligand that selectively binds an ion of interest. The ligand is typically incorporated within a polymer matrix,¹ or directly immobilised on the surface of a transducer². In addition to a suitable ligand, polymer membrane-based chemical sensors normally require an ion-exchanging salt, and if detection is performed using visible optical spectroscopy, a chromo-responsive dye. Such a membrane can contain up to 5 components, i.e. polymer, plasticizer, ligand, ion-exchanger and dye.

There has been great interest in simplifying these chemical sensor mixtures, for example, through the development of plasticizer-free matrices,^{3, 4} covalent attachment of active sensing components to polymer backbone^{3, 5, 6}, and improving the lipophilicity of sensing components⁷⁻⁹.

Interestingly, utilization of more universal components that employ several roles thereby reducing the actual *number* of active components whilst retaining the membrane functionality has not been explored, perhaps because of the lack of suitable materials. Another interesting approach to simplification of sensors is to make them capable of performing simultaneous and/or multianalyte measurements¹⁰⁻¹³. Clearly, through the combination of these strategies, significant simplification of sensor fabrication can be achieved. The unique physical properties of ILs as discussed previously may well allow such simplified fabrication.

In recent years, there has been a considerable effort to optimise ion selective electrodes (ISEs), particularly with respect to improving their limit of detection, and already, the use of ILs that combine the necessary plasticizing and ion-exchanging functions have led to a simplification of ISE membrane formulations¹⁴⁻¹⁸.

The aim of this research is to investigate whether we can employ ILs to further dramatically simplify the formulations used to make effective ion-optode membranes.

We have identified trihexyltetradecylphosphonium dicyanamide [P_{6,6,6,14}][DCA] as an IL capable of fulfilling multiple roles in polymeric optodes thereby dramatically simplifying their composition. First used to impart low viscosity in a new generation of ILs^{19, 20}, [DCA]⁻ has previously been termed a pseudohalide that behaves as a ligand capable of binding to a variety of d-block elements (most notably Cu²⁺, but also Co²⁺, Mn²⁺ and Fe²⁺)²¹⁻²³.

We have utilised this ability in order to demonstrate simultaneous, dual analyte recognition using a very simple, two component (polymer and IL) optical sensing membrane for “proof of concept” experiments.

2.3 Experimental

2.3.1 Chemicals and Materials:

Poly(vinyl chloride) (PVC, high molecular weight), Copper (II) Nitrate trihydrate, Cobalt (II) Nitrate hexahydrate, Potassium Chloride, Europium (III) Chloride, Manganese (II) Chloride, Nickel (II) Nitrate hexahydrate, Aluminum oxide (activated, basic, Brockmann 1) and Tetrahydrofuran (THF) were used as purchased from Sigma-Aldrich® Ireland Ltd.

Trihexyltetradecylphosphonium dicyanamide [$P_{6,6,6,14}$][DCA] was generously donated by Cytec® industries. 10 ml of the ionic liquid was purified by redissolution in 30 mL of acetone followed by treatment with activated charcoal (Darco-G60, Aldrich) at 40 °C overnight. Carbon was removed by filtration through alumina (acidic, Brockmann I) and solvent removed under vacuum.

2.3.2 Instrumentation:

UV/VIS absorption data for the purified IL's were performed using a μ Quant® plate well reader by adding 500 μ L of metal salt solution (if used) to 500 μ L of [$P_{6,6,6,14}$][DCA]. Vibrational spectra were obtained using a Perkin Elmer Spectrum GX FT-IR System® and Perkin Elmer Raman Station 400F®. UV/VIS absorption spectra of all PVC/IL based membranes were performed using a Perkin Elmer Lambda 900 UV/Vis/NIR® spectrometer. Non-contact profilometry was performed using an ALTIMET®-Altisurf 500 profilometer to determine sample thickness.

2.3.3 Membrane Preparation:

Both PVC and [P_{6,6,6,14}][DCA] (1:2 (w/w)) were added to 2 ml THF and stirred until dissolved. The resulting solution was then poured into a glass ring on a glass slide held together by rubber bands. The resulting films were covered for 24 hrs to ensure evaporation of THF .

For multiple analyses, 100 μ L aliquots of the resultant solution can also be streaked over a square, unsilanized microscope cover slide (2.2 cm wide) and left to dry.

In order to generate the optical response, the membranes obtained were then exposed to 500 μ L of the respective metal ion salt solution of desired concentration for 30 mins. The salt solution was then removed using a pipette, enabling the analytical measurements to be performed on the membrane.

2.4 Results and Discussion

2.4.1 Initial IL complexation

In order to examine the co-ordinating abilities of [P_{6,6,6,14}][DCA], we initially exposed the IL to aqueous solutions of Cu(NO₃)₂ and Co(NO₃)₂ independently. This resulted in a strong yellow coloration of the IL in the presence of Cu(NO₃)₂, and a deep blue coloration in the case of Co(NO₃)₂ (after the removal of aqueous layer). Furthermore upon exposure [P_{6,6,6,14}][DCA] to an equimolar mixture of both ions a green colouration was observed due to the co-existence of the two coloured complexes, indicating simultaneous binding of both Co²⁺ and Cu²⁺ ions as seen in figure 2.1. Similar results were obtained by dissolving the solid metal salts in the IL, the corresponding UV-Vis spectra of each sample can be found in figure 2.2.



Figure 2.1: From left to right: IL, IL + $\text{Cu}(\text{NO}_3)_2$ (yellow), IL+ equimolar mixture (green) and IL + $\text{Co}(\text{NO}_3)_2$ (blue).

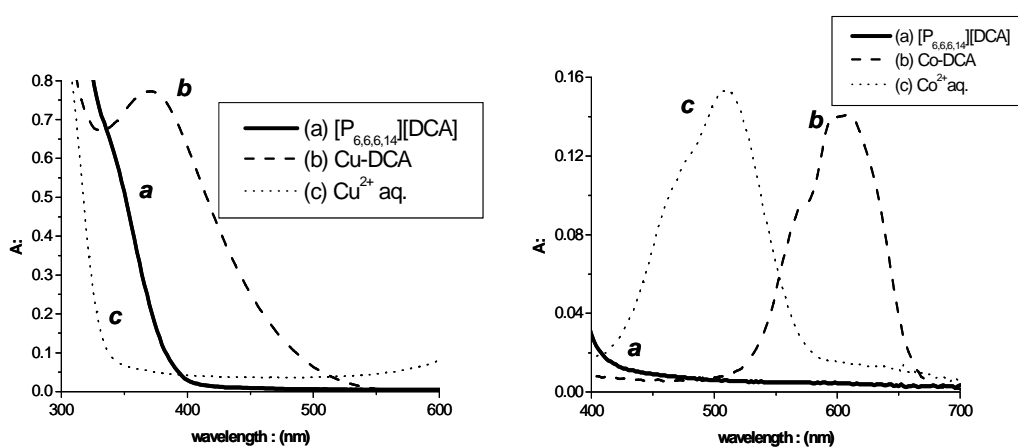


Figure 2.2: Absorption spectra of IL (a), upon complexation with metal ion (b), and the original metal ion solution (c).

2.4.2 Vibrational Spectroscopy Analysis

Our next step was to explore the role of the IL in the complexation process. For this, both IR and Raman Spectroscopy were employed.

Figure 2.3 below depicts the region in the vibrational spectrum where the contribution of the asymmetric nitrile stretch of the anion occurs^{24, 25}.

In all four cases the spectra depict the following: (a) the initial stretch of the IL before complexation ($\nu_{\max}/\text{cm}^{-1} \sim 2125$), (b) the effect of co-ordination of the metal ion to the IL and (c) the spectra of the metal ion aqueous solution.

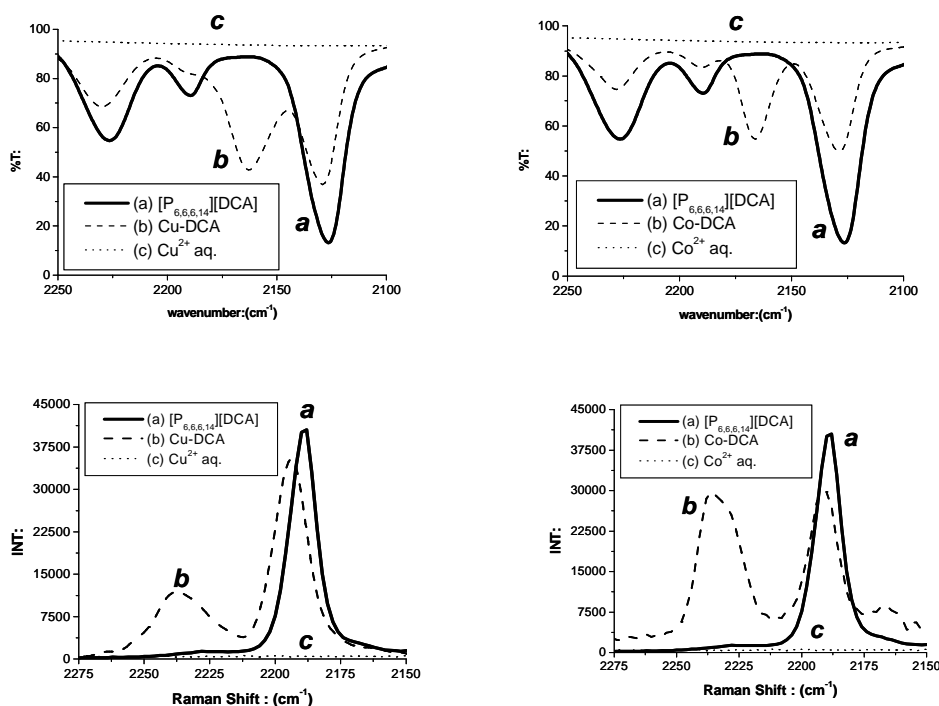


Figure 2.3: Top: IR Spectra obtained of IL (a), upon complexation with metal ion (b) and original metal ion solution (c).

Bottom: Corresponding Raman Spectra.

The IR and Raman co-ordination spectra of nitrile based complexes have been the subject of previous reviews by Nakamoto²⁶ and Griffith²⁷, and further specialised work by Friedrich²⁸. A feature of the spectrum that is agreed upon by all is that the initial nitrile stretch is substantially reduced upon co-ordination, along with the formation of a new stretch at higher frequencies.

The degree of this new stretch is a direct function of the electronegativity of the complexing metal, with increasing metal electronegativity resulting in new stretches at higher frequencies²⁶. Figure 2.3 clearly shows that upon co-ordination a new band appears at $\nu_{\max}/\text{cm}^{-1}$ 2162 (for Cu-DCA) and $\nu_{\max}/\text{cm}^{-1}$ 2166 (for Co-DCA), which we ascribe to the impact of ion-binding on the nitrile stretch. It is important to note that similar effects were not observed upon addition of other ions such as H^+ , K^+ , Eu^{3+} , and Mn^{2+} , suggesting that DCA^- does not complex readily to these ions.

2.4.3 Membrane Preparation

In view of these encouraging results, we explored the possibility of preparing a polymer membrane-based optode using polyvinylchloride (PVC) as a polymer and the IL as a plasticizer. The membrane composition was 33% wt PVC and 66% wt [P_{6,6,6,14}][DCA], a composition typical of PVC-plasticizer-based optodes²⁹.

However, in this case we expected that the IL would fulfil multiple roles – membrane plasticizer, ion-complexing ligand and indicator/transducer dye – thereby simplifying the platform by significant reduction of active components. The resulting membranes were transparent, homogeneous and approximately ~10 µm thick. Exposure of the membranes to the respective metal ion solutions yielded the same colours as obtained with the IL (Figure 2.4).

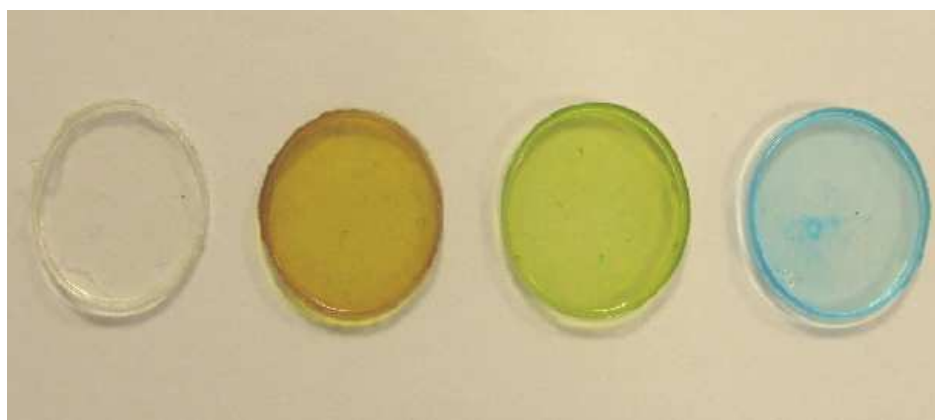


Figure 2.4: Two-component IL-PVC polymeric optode membranes capable of generating 3 distinct optical responses.

As the migration of ions into polymeric optode membranes can occur via one of two distinct mechanisms, co-extraction or ion-exchange²⁹⁻³¹, it is important to determine which is occurring in the case. Ion-exchange mechanisms typically involve the deliberate addition of an ion-exchanging salt, which facilitates ion transfer between both phases. These so called “ionic sites” are typically composed of an

organic, lipophilic anion and a group 1 hydrophilic counter ion. For the cation exchange process the target analyte initially enters the organic phase whilst at the same time the hydrophilic counter ion of the ionic sites migrates out in order to preserve the membrane charge balance. In contrast, the co-extraction mechanism involves simultaneous extraction of the target ion and its counter ion from the aqueous phase into the membrane to preserve charge balance. If the anion from the IL serves as a charged ionophore and binds to a sample ion, the ion-exchange mechanism would only be possible if the cation from the IL migrates into the solution. This mechanism clearly cannot be the case in our system, since the high lipophilicity of the high molecular weight tetraalkylphosphonium cation would not allow it to partition easily into the aqueous phase. Therefore, in this work we assume co-extraction is the prevailing mechanism, although we are currently working on further detailed analysis of the mechanism which will be the subject of a future publication.

2.4.4 Response Times

The response time for these membranes is given by the time necessary to achieve a uniform concentration of optically relevant components. Diffusion of ions into the membrane phase is known as the limiting process. The time needed to achieve 95% of the signal is given in Equation 2.1:

$$t_{95\%} = 1.13 \frac{d^2}{D} \quad (2.1)$$

Where d is the membrane thickness and D is the diffusion coefficient of the ion-ligand complex in a typical PVC-plasticizer based membrane species.

With a membrane thickness of 10 μm and a typical $D \approx 10^{-8} \text{cm}^2/\text{s}$ the $t_{95\%}$ response time should be 100 s^{29} .

Figure 2.5 shows the response of PVC-[P_{6,6,6,14}][DCA] based membranes that have been exposed to 2 ml of $1 \times 10^{-1} \text{M}$ $\text{Cu}(\text{NO}_3)_2$ (left) and $\text{Co}(\text{NO}_3)_2$ (right), respectively. Membrane thickness was found to be approx $193 \mu\text{m}$ (figS1.), the response values obtained for $t_{95\%}$ are 345s and 340s for Cu^{2+} and Co^{2+} , respectively, which is in the expected range for membranes of this thickness.

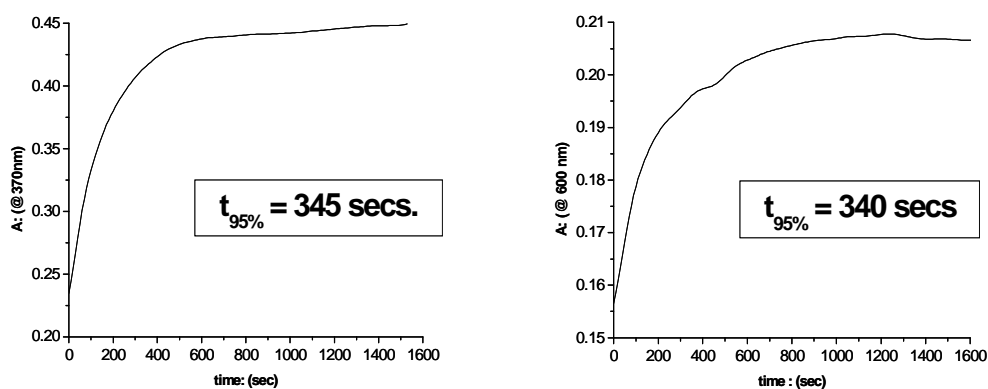


Figure 2.5: Response times obtained for Copper (left) and Cobalt (right) complexation.

2.4.5 Limit of Detection

In order to determine the limit of detection for both analytes, we exposed them to a series of Cu^{2+} and Co^{2+} solutions and measured the UV/Vis absorbance at the maximum absorbance wavelength (370 nm for Cu^{2+} and 600 nm for Co^{2+} ions).

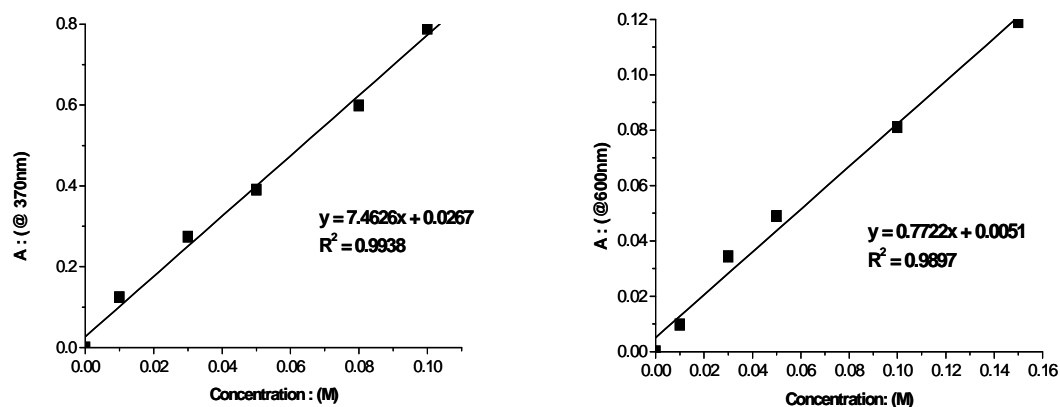


Figure 2.6: Calibration curves obtained for Copper (left) and Cobalt (right) complexation.

The responses of the membranes were fitted to the Beer-Lambert Law (figure 2.6 (above)). From the slopes of the above plots, the estimated extinction coefficients for the membranes were found to be ϵ (Cu-DCA) = 7.46/mol.cm, ϵ (Co-DCA) = 0.772/mol.cm.), at 20 °C. The limit of detection (LOD) was calculated by first obtaining the standard deviation of three blank membrane measurements, and then by adding three times this value to the absorbance of the blank membrane at the individual complexation absorbance maxima³². The calculated limit of detection for Cu-DCA was found to be $7.62 \times 10^{-4}\text{M}$ and $2.91 \times 10^{-4}\text{M}$ for Co-DCA.

2.4.6 Estimation of Stoichiometry and Binding Constants

The binding constants for both ions were calculated using a series of equations based on previously reported theory^{33, 34}. In these equations; α represents the ratio between both the free and initial ligand concentrations (eqn 2.2.).

$$\alpha = \frac{[L]}{[L_{tot}]} = \frac{(A_{complexed} - A)}{(A_{complexed} - A_{uncomplexed})} \quad (2.2)$$

$A_{complexed}$ values were obtained from a series of membranes exposed to metal ion salt solutions (concentrations were the same as for LOD calculation), $A_{uncomplexed}$ by measuring the absorbance of a blank membrane prior to exposure to metal salt solution, and A by measuring the absorbance of the original metal ion aqueous solution. By plotting α against the logarithmic concentration of metal ion present, both the binding constant and stoichiometric ratio can be estimated.

$$[M^{n+}]^m = \frac{1 - \alpha}{nK[L_{tot}]^{n-1} \alpha^n} \quad (2.3)$$

Equation 2.3 was used to determine the results one would obtain from model stoichiometries; i.e. M1:L1, M1:L2 and M2:L1 ((M= metal, L = Ligand)) and these have been plotted against the experimentally obtained values (black dots). In this case $[M^{n+}]^m$ represents a metal ion of charge n , and K can be defined as the equilibrium constant of metal-ligand complexation.

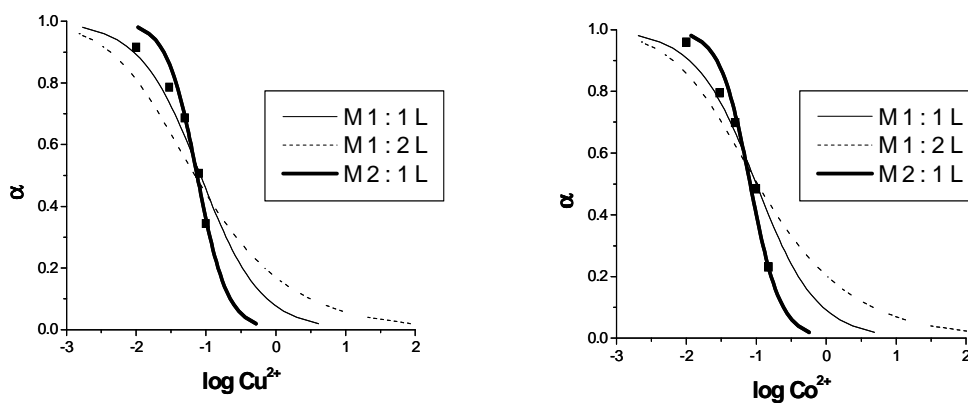


Figure 2.7: Response parameter α as a function of logarithm of Cu^{2+} (left) and Co^{2+} concentration.

Counter-intuitively, the best fit is obtained in the case when $M=2$ and $L=1$ i.e. two metal ions for every DCA^- binding site which represents an obvious charge imbalance. One possible explanation is that this reflects the complex binding nature of the ligand. High delocalization of charge across DCA^- results in many possible binding modes, with Batten et al. stating that up to 8 mono, bi and multidentate coordination modes have been reported³⁵. This rich binding diversity has led to DCA^- being used as a bridging ligand in chain structures, in various 1,2 and 3-D coordinated networks^{36, 37} and in topologies exhibiting magnetic properties³⁸, with some unusual and unexpected binding modes also reported in the latter case³⁹. Therefore, the unusual binding stoichiometry obtained here is not as surprising as would initially thought. The binding constants obtained by fitting the aforementioned curves with experimental data were $\log K = 2.25$ and $\log K = 2.17$ for the Cu^{2+} and Co^{2+} complexes, respectively.

2.4.7 Interfering Ions

To explore the relative affinity of DCA^- for Cu^{2+} and Co^{2+} , and its selectivity against other cations, a series of membranes were exposed to solutions containing either Cu^{2+} or Co^{2+} , and the competing ion in a 1:1 (vol. /vol.) mixture. The concentration of both ions in the mixture was kept at 0.1M.

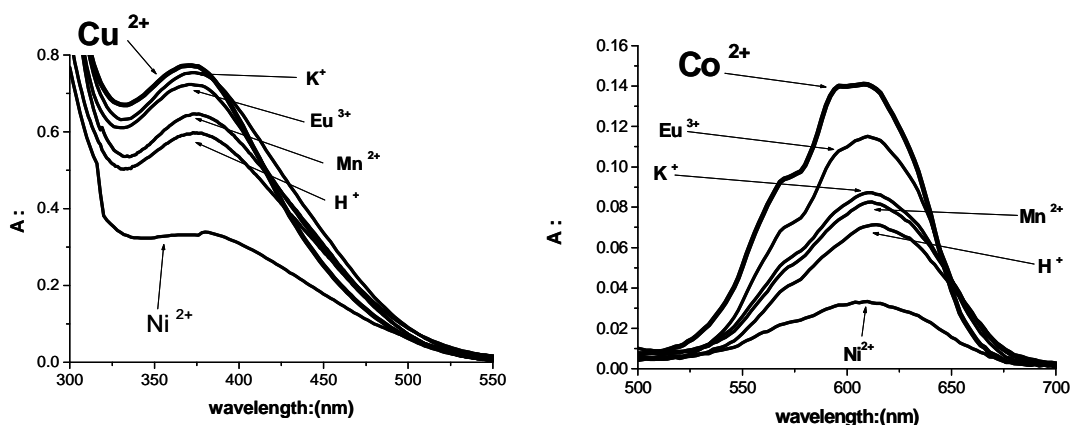


Figure 2.8: Interference spectra obtained for Copper (left) and Cobalt (right) complexation.

The potential interference effects measured were the effects of pH, monovalent cations, other d-block elements such as Ni^{2+} and Mn^{2+} with which DCA^- has been reported to bind, and a trivalent lanthanide cation. From figure 2.8 it can be seen that, of the interferents screened, a reduction in the absorbance occurs in each case, and the order of influence is similar ($\text{Ni}^{2+} \gg \text{H}^+ \gg \text{Mn}^{2+} > \text{K}^+ \approx \text{Eu}^{3+}$). The effect of potential interfering ions was much smaller in the presence of Cu^{2+} ions, than for Co^{2+} ions. Although the binding constants obtained are similar, the calculated extinction coefficient for Cu^{2+} complexes is much higher, which explains the less dramatic interference effects. One result to note is the substantial interference arising from Ni^{2+} in both cases. As stated previously, Ni^{2+} has been reported as forming complexes with $[\text{DCA}]^{-23}$. The addition of a Ni^{2+} to the IL- based membrane however, produces no notable colour which opens the door for an alternate detection technique. This is most likely to be to monitor the inherent electrochemical properties of IL's, given that they have been effectively used as a sensor response previously⁴⁰.

2.4.8 Dual Analyte Recognition

In view of the fact that [P_{6,6,6,14}][DCA] simultaneously complexes both Co²⁺ and Cu²⁺ ions, While the latter might be interpreted as a simple interference, with colorimetric responses that occur at different regions of the visible spectrum, we investigated the possibility of using the membrane for simultaneous detection of both metal ions in mixtures. Interestingly, even though the interferents screened above do, to a greater or lesser extent, reduce the spectral absorbance, they do not generate *new* absorbance peaks.

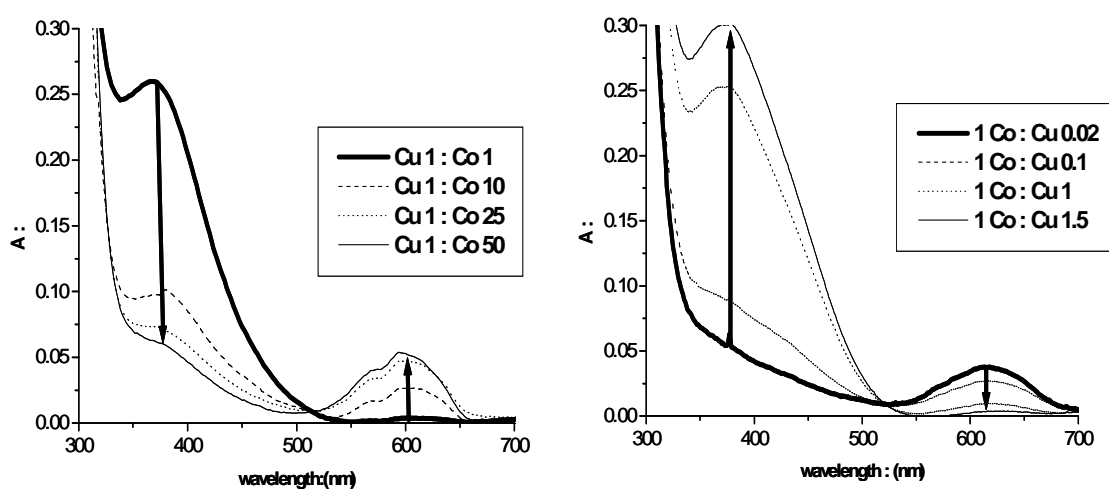


Figure 2.9: Dual-Analyte recognition based on two absorption maxima.

To further characterize this dual-analyte recognition system, membranes were exposed to mixed solutions of Cu²⁺ and Co²⁺ containing various concentration ratios of the two ions. The change in absorbance at the characteristic wavelength for each of the involved ions originates from competition for the same ligand and displacement of bound cations by the competing cation. The importance of this finding is that this two component system is effectively self-indicating. It clearly shows whether ions of interest are present as individual or as a mixture without the need to add a dye (Figure 2.9 above.).

2.5 Conclusion

In short; we have effectively demonstrated how the multifunctional properties of an IL form the basis of a simple, 2-component ion-sensing membrane. [P_{6,6,6,14}][DCA] fulfils roles as diverse ligand, transducer dye and plasticiser; whilst the binding mechanism eliminates the need for an ion-exchanger. The resulting optode is capable of simultaneous recognition of two analytes in a single measurement. The somewhat modest limit of detection and the interferent effect of other ions do highlight the need for improvement if IL's are to be used to sense these ions in real scenarios. In view of the relative ease of synthesis of ILs, the relative ease of incorporating specific functionality into ILs^{41, 42}, and the availability of charged ionophores⁴³⁻⁴⁵ for a wide range of analytes; there is now considerable potential to generate very effective sensing membranes tuned for specific analytes.

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