Synthesis of chloride ion-selective potentiometric sensor based on coordination polymer complex

R Sundaram* & K S Hariprasad

*Department of Chemistry, Science and Humanities, Maamallan Institute of Technology, Sriperumbudur 602 105
Kanchipuram, India
bDepartment of Mechanical & Production Engineering, Sathyabama University,
Chennai 600 119, India
Email: sundaramrsram@rediffmail.com

Received 11 December 2006; revised received 26 June 2007; accepted 12 July 2007

This paper describes the fabrication of an ion-selective electrode in which a 2,5-dihydroxy-p-benzoquinone (DHBQ) is used as the ionophore. The polymers prepared were characterized by elemental analyses, FT-infrared spectra, solid state electrical conductivity studies leading to activation energy, conductance measurements and thermoelectric power measurements. The DC conductance (1/R) values of Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are 8.75×10⁻⁸, 11.8×10⁻⁸, 8.33×10⁻⁸ and 1.28×10⁻⁸ Ω⁻¹, respectively. The current increase exponentially against temperature proves the semiconductive nature. Thermoelectric power (TEP) measurements showed the sign of the seebeck coefficient which was positive in the temperature range and hence it was concluded that the majority carriers are of n-type. The low activation energy is interpreted in terms of intermediate trap levels. The main advantage of the electrode is that it is mechanically stable up to 3 years. The electrode shows a linear response in the range of 2.5×10⁻⁵ – 0.5×10⁻¹ mol dm⁻³. The response time of the electrode is 30 s. The pH range at which the electrode works is 3.8 to 6.8. The electrode was found to be selective towards chloride ion in the presence of ions like Na⁺, Ca²⁺, Mn²⁺, Fe³⁺, Co²⁺, Cu²⁺, Zn²⁺, CH₃COO⁻, NO₃⁻, SO₄²⁻, Br⁻ and NO₂⁻.

Keywords: Coordination polymers, Polychelates, Electrical conductance measurement

IPC Code(s): C08B1/00

A coordination polymer is the one in which a metal ion is coordinated with an organic substance to form a polymer in which there is a metal atom or ion for each monomer unit[^1][^1]. The products are best described by the term polymeric chelates, which is capable of breaking the coordination bond but would not rupture the polymer backbone[^8]. The coordination bonds are an integral part of the polymer backbone. Number of organic materials have been prepared which act as semiconductors to which the energy gap between the valence band and conduction band lie in the required range[^5][^6]. The fact that the metal-ligand bonds are formed reversibly and the types of metal are most likely to form suitable polymers are the advantages[^7] of polymers. The polymer complexes normally possess the intra-molecular migration of electron and hence the carrier mobility[^8].

Ion-selective electrodes (ISEs) provide a convenient and quick analytical procedure for the estimation of ions in solutions which may be turbid, coloured and contain additives[^9][^10]. ISEs of different types are reported in the literature[^11][^12]. Polymeric membrane ISEs provide one of the most powerful sensing methods as it is possible to select various sensory elements according to the shape and size of the target ion[^13]. Most membranes in polymer membrane ISEs are based on a polyvinylchloride matrix[^14][^15]. Polystyrene based electrodes were found to be inert, mechanically stable with long life and low response time[^16][^17]. A number of attempts have been made to develop chloride ISEs which are based on conducting polymers[^18][^19], polyvinyl chloride[^20][^24].

The current interest in coordination polymers comes largely from the fact that there is a growing need for polymers of great stability and that, in many cases, organic material is stabilized against thermal or chemical attack by coordination with a metal ion[^25]. The polychelates of bis(mercaptoacetamide)-p-phenylenediamine[^26] [BMAPD] with bivalent Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions and the
quadridentate ligand 4,4'-dihydroxy-3,3'-diacetylbiphenyl-2,3-butanedionedihydrazone\textsuperscript{27} (DDBBD) with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been reported. The chelate polymers of bivalent Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with the Schiff base of 5,5'-methylenbis(3-nitrosalicylaldehyde) with 1,4-diaminobutane was reported\textsuperscript{28}. The iodine doped semiconducting chelate polymers of bis-mercaptopacetamide ethylene diamine have also been reported\textsuperscript{29,30}. In the present investigation, a sensitive electrode selective to chloride ion has been developed. The fabricated electrode has a stable shelf life of about three years and is inert towards most of the transition metal ions and a variety of anions. A transition metal complex of 2,5-dihydroxy-p-benzoquinone (DHBQ) polymer has been developed as ionophore in the fabrication of the electrode.

**Experimental Procedure**

**Reagents and Analyses**

All reagents were of analytical reagent grade and were used without further purification. Iron(III) chloride, cobalt(II) nitrate, nickel(II) sulphate, copper(II) sulphate, 2,5-dihydroxy-p-benzoquinone (DHBQ) and methanol were products of Merck. The synthesis of the coordination polymers of Fe(III), Co(II), Ni(II) and Cu(II) with 2,5-dihydroxy-p-benzoquinone (DHBQ) were prepared by the conventional solution route method i.e., by the interaction of respective constituents in methanol. Iron, cobalt, nickel and copper were determined\textsuperscript{31} by wet chemical analyses. FT-IR spectra were recorded in the 4000–400 cm\textsuperscript{-1} region as KBr matrix on a Bruker IFS 66V spectrophotometer.

**Fabrication of chloride ion-selective electrode**

Coordination polymer complex was developed as the electro active material (ionophore) for the fabrication of the chloride ISEs. FeCl\textsubscript{3} or Co(NO\textsubscript{3})\textsubscript{2}.5H\textsubscript{2}O or NiSO\textsubscript{4}.7H\textsubscript{2}O or CuSO\textsubscript{4}.5H\textsubscript{2}O (1.62, 2.91, 2.37 and 2.49 g in 25 mL of methanol respectively) was mixed with DHBQ (1.40 g in 25 mL of methanol) in a round bottomed flask, fitted with a water condenser. This alcoholic mixture was refluxed on a water bath for 4 h. The black precipitate was filtered, washed with hot water and methanol to remove the unreacted reactants and dried. The yield was found to be 74%.

About 100 mg of dried electro active material was mixed with 400 mg of araldite and the paste was spread over a Whatman No. 41 filter paper to 0.1 mm thickness and air-dried for 48 h. It was separated from the membrane by dipping it in a solution of CoCl\textsubscript{2} and was cut to required size and then attached to one end of a glass tube with araldite. The tube was filled with 0.1 mol dm\textsuperscript{-3} CoCl\textsubscript{2} solution and kept immersed in the CoCl\textsubscript{2} solution of same strength for 24 h. Potentials were determined by direct potentiometry at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode. The detailed cell setup is shown in Fig. 1.

The emf of the cell set-up was measured using an Aplab Digital Multimeter at room temperature. Response behaviour of the electrode was studied by measuring the potential of the electrode at different concentrations of chloride ion. The pH dependence of the electrode potential was studied by varying the pH of the chloride solution of fixed concentration with buffer solutions. Interference studies were also carried out by mixing the chloride solution of fixed concentration (0.05 mol dm\textsuperscript{-3}) with solutions of different concentrations of foreign ions like Na\textsuperscript{+}, Ca(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), CH\textsubscript{3}COO\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2–}, Br\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-} and measuring the potentials one after another.

**Conductivity measurements**

Field dependent conductivity studies on the samples were carried out using DC two-probe method\textsuperscript{32}. The samples were mounted on a precleaned glass slide and two thin copper wires (1.4 mm diameter) were fixed by using silver paint (GE Thorsen). The electrode distance maintained to be around 1-2 mm and was measured accurately by a

![Fig. 1—Cell setup for interference study.](image-url)
travelling microscope. The experimental setup was electrically connected to a DC power supply (Aplab L3202) and a Pico-ammeter (Keithley 485) in series. In order to study the temperature dependence of conductivity, the sample was kept inside a Pyrex cylinder of 5 cm diameter and 75 cm length with kanthal aluminium wire uniformly wound around it. The ends of the kanthal wires were connected to a variac for heating. A K-type thermocouple (Cr/Al) whose hot junction located in the close proximity was used for monitoring the temperature on the sample accurately. The electrodes of the sample were connected to the DC power supply and the pico-ammeter in series as before. Given the high resistivity of the materials under investigation, the potential inaccuracy due to contact resistance is assumed to be negligible.

**Thermoelectric power (TEP) measurements**

For TEP measurements, the sample disc along with the hot junction of two K-type thermocouples pressed against the flat surfaces were sandwiched between the two flat ends of one-end-closed concentric quartz tubes. Two circular platinum discs sandwiched between the thermocouple and the same sample on either face served as the electrodes. The necessary mechanical pressure was exerted by two springs, which pulled the tubes together near their open ends at the mouth of the furnace. A resistance wound tubular furnace of vertical configuration was used for these measurements. The temperature profile of the furnace was determined prior to the experiment by maintaining a central temperature of about 1000°C using a PID-type proportional power controller along with an independent thermocouple. It was found that at a depth of 180 to 220 mm from the mouth of the furnace of dimension 450 mm in height and 40 mm ID, there existed a considerable linear temperature gradient, which could be utilized for the experiments. This gradient was used for TEP measurements by locating the thermocell in this zone of the furnace. The thermo-emf as well as the thermocouple output was measured using a high impedance digital multimeter (Solartron DMM 7150). The thermo-emf was measured in ambient air by connecting the identical chromel leads of the two thermocouples. The TEP was measured as stated above by exploiting the linear temperature gradient existing in the furnace at a location that could give rise to a temperature gradient of 10°C between the two faces of the sample. The thermo cell was located in the constant temperature (∓1°C) zone of the same furnace assembly for generating a correction for the isothermal contact potential between chromel/Pt cum Pt/chromel.

**Results and Discussion**

The elemental analysis suggested the proposed composition of the complexes. The interaction between metal ions and bridging ligands in solution leads to the formation of coordination polymers in which the chelated metal ions are bridged by ligand molecules. The IR spectral data indicated the presence of coordinated water molecules and phenolic OH (Fig. 2). Fe(III)-DHBQ shows a broad weak band in the high frequency region assigned to the presence of coordinated water and is further supported by the presence of a band at 690 cm⁻¹. The band at 1204 cm⁻¹ is characteristic of phenolic OH. Shift of C=O frequencies by approximately 50 cm⁻¹ to lower frequency indicates the involvement of C=O in chelation. The peak at 1664 cm⁻¹ is highly characteristic of 1,4-quinones. The peaks at 3062 and 1596 cm⁻¹ are assigned to aromatic C-H and C=C stretching, respectively. The peak at 1367 cm⁻¹ is assigned to C-O stretching and the shift of C-O band to lower frequency further supports the participation of the phenolic OH in coordination. The peak at 876 cm⁻¹ is assigned to aromatic C-H bending. In the case of Co(II)-DHBQ, the broad band around 3380 cm⁻¹ is assigned to coordinated water and the band at 1215 cm⁻¹ is characteristic corresponding to phenolic OH. The fingerprint of 1,4-quinones is observed as a weak band at 1652 cm⁻¹. A sharp, but a broad band is observed at 3385 cm⁻¹ in the case of Ni(II)-DHBQ and is assigned to coordinated water. The sharp peak at 1590 and 1604 cm⁻¹ corresponding to Ni(II)-DHBQ and Co(II)-DHBQ, respectively, assigned to C=O, indicates the strong involvement of C=O bond in the coordination. In Cu(II)-DHBQ, the peaks at 1220, 1380 and 890 cm⁻¹ are assigned to phenolic OH, C-O stretching and aromatic C-H bending, respectively.

**Response behaviour of electrode**

Electrodes were constructed with different proportions of the ionophore and the binder, it was found that stability and slope are highly favouring a proportion of 1:4. Hence, further work was carried out using an electrode of this composition. Stable potentials were developed within a time span of 30 s, when the developed sensor is placed in chloride solution. The mechanism may be a smooth exchange of Cl⁻ ions between the complex and the solution. The
Electrode potentials show a linear response in the range of $2.5 \times 10^{-5} - 0.5 \times 10^{-1}$ mol dm$^{-3}$ of Cl$^-$ concentration. The slope of $E$ versus $-\log$ Cl$^-$ is 57.7 mV (Fig. 3), which indicates the Nerstian nature of the electrode. The slope remained constant for about four weeks even after continuous use and the linear response was maintained for about three months, although absolute potential values changed slightly (<5 mV), as is commonly observed with ISEs\textsuperscript{16}. The response time of the membrane was measured at various concentrations of test solutions. Stable potential was obtained within 30 s which remained unaltered up to 7 min. Potentials were determined for five different concentrations of chloride ion and the percentage error and precision parameters were calculated (Table 1). The results presented in Table 1 reveal that the method is accurate and precise.

**Effect of pH**

The pH dependence of the electrode potential was also studied (Fig. 4). The potential remains constant in the pH range of 3.8 – 6.8. This may be taken as the working range of pH of the electrode. The concentration of chloride ion taken was $0.5 \times 10^{-2}$ mol dm$^{-3}$ for these studies.

![FT-IR spectrum of coordination polymer complex in KBr matrix: (a) Fe(III)-DHBQ, (b) Co(II)-DHBQ, (c) Ni(II)-DHBQ and (d) Cu(II)-DHBQ.](image)

![Potentiometric responses of membrane towards different concentrations of chloride ion.](image)

![Potentiometric responses of membrane towards chloride ion solution $(0.5 \times 10^{-3}$ mol dm$^{-3}$) at different pH values.](image)
Table 1—Determination of chloride

<table>
<thead>
<tr>
<th>[Cl–] (mol dm–3)</th>
<th>–log[Cl–]</th>
<th>E (mV)</th>
<th>–log[Cl–]</th>
<th>[Cl–] Error</th>
<th>S.D. (%)</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 × 10–1</td>
<td>0.823</td>
<td>54</td>
<td>0.822</td>
<td>1.50 × 10–1</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>1.5 × 10–2</td>
<td>1.823</td>
<td>116</td>
<td>1.831</td>
<td>1.47 × 10–1</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>1.5 × 10–3</td>
<td>2.823</td>
<td>172</td>
<td>2.819</td>
<td>1.51 × 10–1</td>
<td>1.00</td>
<td>0.002</td>
</tr>
<tr>
<td>1.5 × 10–4</td>
<td>3.823</td>
<td>232</td>
<td>3.818</td>
<td>1.52 × 10–1</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>1.5 × 10–5</td>
<td>4.823</td>
<td>293</td>
<td>4.825</td>
<td>1.49 × 10–1</td>
<td>0.33</td>
<td></td>
</tr>
</tbody>
</table>

Interference studies

The influence of interfering ions on the response behaviour of ion-selective electrode is usually described in terms of selectivity coefficient. The potential response of the chloride ion sensor to different ions has been investigated by determining the selectivity coefficient of the electrode ($K_{i,j}^{pot}$) using a transformation of the Nikolski – Eizenman (N–E) equation\(^{37}\). Its value is determined by the ability of the disturbing ion to affect the electrode potential relative to that of the main ion. The resulting $K_{i,j}^{pot}$ values are summarized in Table 2. The results show that presence of Na\(^+\), Ca\(^{2+}\), Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), CH\(_3\)COO\(^-\), NO\(_3^–\), SO\(_4^{2–}\), Br\(^–\) and NO\(_2^–\) do not affect the selectivity of the chloride ion electrode significantly over the concentration range studied.

Conductivity measurements

When the field dependent conductivity studies were carried out on the samples, current increased linearly suggesting the ohmic nature of the samples (Figs 5a–5d). This further proves that the work function of the electrode material, silver, is higher than the samples and hence no charge carriers are injected at the electrodes. Hence, silver can be used as the electrode contact. The DC conductance ($\frac{1}{R}$) values of Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are 8.75×10\(^{-8}\), 11.8×10\(^{-8}\), 8.33×10\(^{-8}\) and 1.28×10\(^{-8}\) Ω\(^{-1}\), respectively. Among the four set of samples, the conductance of Cu(II)-DHBQ is the lowest and highest conductance is exhibited by Co(II)-DHBQ at room temperature. The conductance range lies in the range of a semiconductor and hence temperature variation studies were carried out to find out the activation energy for the semiconductors in the present investigation.

The plots (Figs 6a-d) of the temperature dependence of conductance for the samples along with least square regression fitting in the temperature range of 100-400°C, are used to evaluate the activation energy for the DC conductance. The activation energy ($E_a$) values of Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are 0.69, 0.29, 0.26 and 1.14 eV, respectively. The samples were heated in vacuum at 200°C for 6 h to remove the adsorbed gases and moisture. The ln$I$ versus $10^3/T$ plot was found to be a straight line with negative slope from which the activation energy was calculated\(^{38,39}\). The thermal activation energy for electrical conduction for Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ was found to be in the following order: Ni(II)-DHBQ < Co(II)-DHBQ < Fe(III)-DHBQ < Cu(II)-DHBQ. From this it can be inferred that Cu(II)-DHBQ which has the lowest conductance (1.28×10\(^{-8}\) Ω\(^{-1}\)) has the maximum activation energy. The thermal activation energy for electrical conduction in semiconductors is usually interpreted in one of two possible ways viz., half the band gap (material presumed intrinsic) or the trap level (material presumed extrinsic). In physical terms one of the requirements of activation energy to be manifested in
Fig. 5—Field versus current plot of coordination polymer complexes: (a) Fe(III)-DHBQ, (b) Co(II)-DHBQ, (c) Ni(II)-DHBQ and (d) Cu(II)-DHBQ.

Fig. 6—ln I versus $10^3/T$ plot of coordination polymer complexes: (a) Fe(III)-DHBQ, (b) Co(II)-DHBQ, (c) Ni(II)-DHBQ and (d) Cu(II)-DHBQ.
electrical conduction is that specific energy levels must contribute to partition functions of the electrons or holes. At each temperature there should be one such level for each carrier. These levels are called dominant levels. In narrow band gap materials the dominant levels tend to be the transport (valence and conduction) bands whereas in wider band gap materials localized levels within the gap tend to be dominant. For the electrical conduction process, carriers must reside in one of the transport bands. Thus, the activation energy for electrical conduction should involve the energy required to raise the carriers from their dominant levels to their transport bands. Moreover, it is also important to find exactly the nature of conduction mechanism in polymeric materials. In general, polymeric materials containing mixture of amorphous or less ordered carriers was the dominant conduction mechanism in these investigations and the charge carriers move by a thermally activated hopping process.

The TEP was obtained by correcting for the chromel to Pt contact potential using the expression $E_{\text{chromel, Pt}} / \text{mV} = -10.43 + 0.03371 T \text{(K)}$. At each temperature, the contact potential was subtracted from the thermo-emf obtained and the TEP ($\theta_{\text{corr}}$) was calculated. The average value of TEP corrected at 250°C is taken for discussion for the purpose of brevity. The Seebeck coefficient was found to be positive in the entire temperature range suggesting the nature of the majority carriers to be $n$-type. The $\theta$ value at 250°C, for Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are 0.15, 0.27, 0.25 and 0.28 mV, respectively. The hot terminal was kept as positive and the cold terminal was maintained at negative. The $n$-type conduction can be explained in the light of the fact that the electron rich 1,4-quinone ring is coordinated to the metal, which in turn is attached to another 1,4-quinone ring and as a result this provides a smooth channel for the flow of electrons.

The low activation energy of the samples is interpreted in terms of intermediate trap levels. Though the conductance values for Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ lies in the semiconductor range but the activation energy values are quite low. Hence, it is understood that the normal valence to conduction band mechanism cannot be applied to these materials in the temperature range of 100-300°C, but the transition is between the intermediate trap levels contributed by impurities and interstitials.

### Table 3—Determination of Cl⁻ in industrial effluent and natural water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present method</th>
<th>Argentometric method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloride found*</td>
<td>S.D*</td>
</tr>
<tr>
<td>Industrial effluent</td>
<td>240</td>
<td>0.04</td>
</tr>
<tr>
<td>Drinking water</td>
<td>48</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Average of 6 replicates

**Application studies**

The presently developed sensor was used for the determination of chloride ion present in treated industrial effluent from a fertilizer industry and also in a drinking water sample. The results have been compared with the standard argentometric method and the results are presented in Table 3. The results show that the method is reliable, precise and accurate. The sensor may be recommended for the routine analysis of Cl⁻ in industrial effluents.

**Conclusion**

Coordination polymers of Fe(III), Co(II), Ni(II) and Cu(II) with 2,5-dihydroxy-p-benzoquinone (DHBQ) were prepared by the literature procedure, by the interaction of the respective constituents in methanol. The samples were characterized by infra red spectroscopy. The samples were subjected to DC two-probe electrical conductivity and thermoelectric power measurements to infer the transport properties. The current increase with applied field was found to be a straight line indicating the ohmic nature and further proving that the work function of the samples is less than the silver electrodes. The DC conductance ($1/R$) values of Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are $8.75 \times 10^{-8}$, $11.8 \times 10^{-8}$, $8.33 \times 10^{-8}$ and $1.28 \times 10^{-8} \Omega^{-1}$ respectively. The plot of $\ln I$ versus $10^3/T$ was found to be a straight line with a negative slope from which the activation energy was calculated. The activation energy for Fe(III)-DHBQ, Co(II)-DHBQ, Ni(II)-DHBQ and Cu(II)-DHBQ are determined to be 0.69, 0.29, 0.26 and 1.14 eV respectively. Thermoelectric power measurements (TEP) were carried out on the samples using the cell, Pt/sample/Pt, to determine the principle conducting species (majority carriers). Necessary corrections were made for chromel/Pt contact resistance. The sign
of the Seebeck coefficient was positive in the temperature range studied and hence it was concluded that the majority carriers are of \( n \)-type. The low activation energy is interpreted in terms of intermediate trap levels.

A chloride ion-selective electrode, based on the polymeric Schiff base complex of amino methylated polystyrene and salicylaldehyde is developed. The electrode works at a convenient \( p \)H range of 3.8-6.8 without interference from other ions. Determinations can be carried out at a concentration range of \( 2.5 \times 10^{-5} \) – \( 0.5 \times 10^{-3} \) mol dm\(^{-3}\). A quick response time of less than 30 s and a comparatively long stable shelf life of 3 years (Orion ion meter, M/s Thermo ion, USA) are the striking advantages of the presently developed electrode. Further, the developed electrode is highly convenient, as there is no need of any plasticizer or solvent for its fabrication.

Acknowledgement

The authors are thankful to Honorable Chairman Dr Jeppiaar, Jeppiaar Educational Trust, for his support and encouragement. They thank Dr. J. Abbas Mohaideen, Principal, Maamallan Institute of Technology, Sriperumbudur and Dr. K. Palanikumar, Principal, SRR Engineering College, Chennai for their valuable suggestions.

References