

A copper-selective electrode based on bis(acetylaceton)propylenediimine

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Abstract

The potentiometric response characteristics of Cu²⁺-selective electrodes based on bis(acetylaceton)propylenediimine (**I**) combined with anion localizing agent (sodium tetraphenyl borate (NaTPB)) and solvent mediators (dibutyl butyl phosphonate (DBBP), tri-*n*-butyl phosphate (TBP) and chloronaphthalene (CN)) were investigated. The best results for Cu²⁺ sensing was obtained for the electrode membrane containing PVC, **I**, DBBP and NaTPB in composition 5:100:200:6 (**I**:PVC:DBBP:NaTPB) (w/w; mg), where the electrode had a Nernstian response (30.0 mV/decade) to Cu²⁺ within the concentration range 1.0×10^{-5} to 1.0×10^{-1} M and detection limit of 0.5 ppm. The operational pH range of the electrode was 3.3–7.0. Selectivity characteristic of the proposed electrode was also assessed by calculating $K_{A,B}^{Pot}$ using fixed interference method matched potential method. The sensor has been successfully used in the potentiometric titration of copper ions with EDTA.

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1. Introduction

Determination of copper assumes importance in view of its widespread occurrence in environmental samples. As such large concentrations of copper can be tolerated by human beings, however, excessive dosage and long term exposure may cause irritation of the nose, mouth and eyes and it causes headache, stomach ache, dizziness, vomiting and diarrhea. Intentionally high uptakes can result in Wilson disease. Recently, ion sensors are being frequently used in the analysis of metallic constituents as these devices make measurements feasible which are otherwise difficult to monitor and perform efficiently. A number of attempts have been made to develop Cu²⁺ selective sensors [1–13], but most of them suffer from poor selectivity, narrow concentration range, non-Nernstian

response, long response time, and poor reproducibility. Efforts are, therefore, still continued to develop selective and sensitive sensor systems. The primary requirement for the preparation of an ion sensor is that the electroactive material to be used in the membranes should exhibit stronger affinity for a particular metal ion. The limited availability of such materials makes it difficult to develop efficient sensors.

Schiff bases or imines, R₂C=NR– are the condensation products of aldehydes and ketones reacting with primary amines and these ligands are well known to form stable complexes of metals. Sensors comprising Schiff base as electroactive ingredient have been reported to exhibit excellent selectivity for Cu²⁺ ions. Schiff base upon deprotonation form complexes with Cu²⁺, which act as charge carriers in the membrane matrix. In the present communication a Schiff base, bis(acetylaceton)propylenediimine, has been explored as suitable ionophore to develop a selective membrane sensor for copper ions and results are compiled in the present communication.

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2. Experimental

2.1. Reagents

All reagents used in the investigations were of analytical reagent grade (BDH, UK). Doubly distilled water was used for preparing all aqueous solutions. Anion excluder, Sodium tetraphenyl borate (NaTPB) and tri-*n*-butylphosphate (TBP) from BDH (England), dibutyl butyl phosphonate (DBBP) from Mobil (USA) and chloronaphthalene (CN) from Merck (Germany) were used. Bis(acetylaceton)propylenediimine (**I**) was synthesized by the published procedure [14].

2.2. Apparatus

The potential measurements were carried out at 25 ± 0.1 °C with a digital pH meter/millivoltmeter (Toshniwal Inst. Mfg. Pvt. Ltd., Ajmer, India). pH measurements were made on a digital pH meter (LabIndia pH Conmeter, India). Glass electrodes as pH electrode and calomel as reference electrodes were used.

2.3. Electrode preparation

The membranes were prepared as suggested by Craggs et al. [15]. Varying amounts of the ionophore (**I**) along with appropriate amount of high molecular weight PVC were dissolved in ~20 mL tetrahydrofuran (THF). The mixture was vigorously shaken and after removing the air bubbles, it was poured into rings made of polyacrylates, which were placed on a smooth glass plate and the solution was allowed to evaporate at room temperature. After 48 h, transparent membrane of 5 mm diameter was cut, attached to a "Pyrex" glass tube with the help of Araldite and immersed in the Cu^{2+} solution for equilibration. For studying the effect of solvent mediators varying amounts of these compounds were added to the solution prior to pouring it into the acrylic rings. The ratio of membrane ingredients was optimized after a good deal of experimentation to provide membranes that generate reproducible, low noise and stable potentials. Further, the membranes having only PVC as membrane ingredient (blank membranes) were also prepared to observe whether any background potentials being produced due to binding material or not. The membranes prepared above were equilibrated in copper nitrate solutions of varying concentrations for different

periods of time. Satisfactory equilibration was achieved with 0.5 M Cu^{2+} solution in a contact time of 3 days.

2.4. EMF measurements

All the potential measurements were carried out at 25 ± 0.1 °C temperature by using the following cell assembly.

Internal reference electrode SCE	Cu(II) 0.1 M (Internal solution)	Membrane	Test solution (External solution)	External reference electrode SCE
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The saturated calomel electrodes (SCE) were used as internal and external reference electrodes. The concentration of the metal ion in the test solutions varied from 1.0×10^{-6} to 1.0×10^{-1} M.

3. Results and discussion

3.1. Working concentration range and slope

Investigations revealed that proper equilibration of the membranes was achieved, when these were immersed in a solution of 0.5 M Cu^{2+} for 3 days. Since the nature of plasticizers influences the dielectric constant of the membrane, the mobility of the ionophore molecule and state of ligand [16], it is expected that the plasticizers play a key role in determining the ion-selective characteristics. So in the present work, three plasticizers viz., DBBP, TBP and CN were added in varying amount to the membrane matrix and ion-selective characteristics were studied (Table 1). Also, the optimization of perm-selectivity of the membrane sensor is known to be highly dependent on the incorporation of additional components [16], therefore, NaTPB was also added to the membrane components for better results. A perusal of data from Table 1 and Fig. 1 shows that membrane without plasticizer exhibited a linear response in the concentration range 2.5×10^{-4} to 1.0×10^{-1} M with a slope of 27.0 mV/decade of activity of Cu^{2+} . In the present study addition of plasticizer improves the response characteristics and the best response was exhibited by the membrane (no. 2) incorporating **I**, DBBP and NaTPB in the ratio 5:100:200:6 (**I**:PVC:DBBP:NaTPB) (w/w; mg). The working concentration range of membrane no. 2 is

Table 1

Composition of PVC based membranes of bis(acetylaceton)propylenediimine (**I**) and performance characteristics of Cu^{2+} selective electrode based on them

Sensor/ membrane no.	Composition of the membrane (w/w)						Working concentration range (M)	Slope (± 0.6 mV/ decade of activity)	Response time (s)
	(I)	DBBP	TBP	CN	NaTPB	PVC			
1	5.0	–	–	–	6	100	2.5×10^{-4} to 1.0×10^{-1}	27.0	40
2	5.0	200	–	–	6	100	1.0×10^{-5} to 1.0×10^{-1}	30.0	10
3	5.0	–	200	–	6	100	5.0×10^{-5} to 1.0×10^{-1}	31.5	20
4	5.0	–	–	200	6	100	8.9×10^{-5} to 1.0×10^{-1}	29.0	15

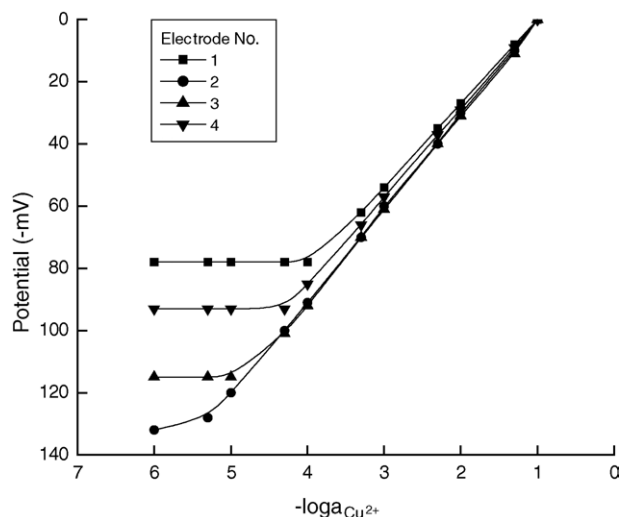


Fig. 1. Variation of membrane potential of PVC based membranes of (I) with varying concentrations of Cu²⁺ ions, without plasticizer (1); with DBBP (2); with TBP (3) and with CN (4).

1.0×10^{-5} to 1.0×10^{-1} M with a slope of 30.0 mV/decade and limit of detection 0.5 ppm. Membrane no. 3 with TBP showed linearity in the concentration range 5.0×10^{-5} to 1.0×10^{-1} M with a slope of 31.5 mV/decade while the membrane no. 4 with CN worked comparatively in the narrow range 8.9×10^{-5} to 1.0×10^{-1} M. Thus, the membrane no. 2 was chosen for further studies.

3.2. Response and lifetime

Response time is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the instant at which the potential has reached 90% of the final value [17]. The response time for the electrode no. 1 was 40 s and the addition of plasticizers also shortened the response time by 10–30 s. The best response time (10 s) was recorded for the membrane having DBBP as plasticizer.

The lifetime of the proposed electrode was carried out by performing periodic calibration with standard solutions and calculating the response and slope over the range 1.0×10^{-6} to 1.0×10^{-1} M Cu²⁺ solution and it was found that electrode worked well over the period of more than 3 months without showing any significant divergence in concentration range, slope and response time. During non-usage, the electrodes were stored in air and before use; they were re-equilibrated by dipping in 0.5 M Cu²⁺ solution for 3 days.

3.3. pH dependence and non-aqueous effect

The effect of pH of the copper nitrate test solutions (1.0×10^{-3} and 1.0×10^{-4} M) on the sensor potential was investigated by following the potential variation over the pH range 2.0–8.0. The influence of pH on the response of PVC

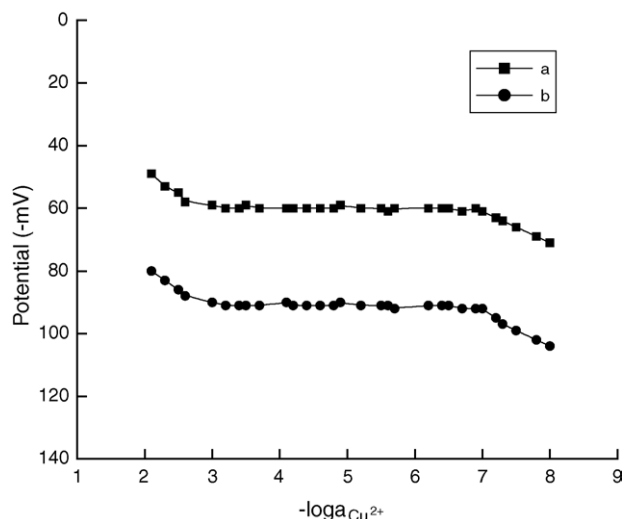


Fig. 2. Effect of pH on potential of membrane no. 2 at [Cu²⁺] = 1.0×10^{-3} M (a); 1.0×10^{-4} M (b).

membrane electrode is shown in Fig. 2 and it depicts the potential remain constant from pH 3.3–7.0. The same was taken as the operational pH range.

The functioning of the sensor was also investigated in partially non-aqueous medium using methanol-water and acetone-water mixtures (Table 2) as real samples may also contain non-aqueous contents. It was found that the sensor assembly works well in non-aqueous media having a 20% (v/v) alcoholic content without showing any appreciable change in the working concentration range or slope. Above 20% organic phase, drift in the potential may be probably due to complex formation between Cu²⁺ and organic molecules or leaching of the ionophore at higher organic content.

3.4. Potentiometric selectivity

Selectivity is an important characteristic, which defines the nature of the device and the range to which it may be successfully employed. It is measured in terms of potentiometric selectivity coefficient ($K_{i,j}^{Pot}$) which may be evaluated

Table 2
Effect of partially non-aqueous media on the working of Cu²⁺ selective sensor (no. 2)

Non-aqueous content (% v/v)	Slope (± 0.6 mV/decade of activity)	Working concentration range (M)
0	30.0	1.0×10^{-5} to 1.0×10^{-1}
Methanol		
10	30.0	1.0×10^{-5} to 1.0×10^{-1}
20	30.0	1.2×10^{-5} to 1.0×10^{-1}
25	31.0	2.9×10^{-5} to 1.0×10^{-1}
Acetone		
10	30.0	1.0×10^{-5} to 1.0×10^{-1}
20	30.0	1.0×10^{-5} to 1.0×10^{-1}
25	30.5	3.0×10^{-5} to 1.0×10^{-1}

Table 3

Selectivity coefficient values ($K_{i,j}^{\text{Pot}}$) for Cu^{2+} selective sensor as obtained by Fixed Interference Method (FIM) and Matched Potential Method (MPM) for various interfering ions at concentration 1.0×10^{-2} M

Interfering ion (B)	Selectivity coefficient, $K_{i,j}^{\text{Pot}}$	
	FIM	MPM
Na^+	2.4×10^{-2}	2.0×10^{-2}
K^+	3.8×10^{-2}	3.5×10^{-2}
NH_4^+	2.6×10^{-2}	2.5×10^{-2}
Li^+	2.0×10^{-2}	2.3×10^{-2}
Ag^+	2.1×10^{-2}	2.3×10^{-2}
Ca^{2+}	3.3×10^{-2}	3.0×10^{-2}
Cd^{2+}	1.2×10^{-1}	1.0×10^{-1}
Zn^{2+}	3.5×10^{-2}	3.3×10^{-2}
Co^{2+}	2.2×10^{-2}	1.9×10^{-2}
Ni^{2+}	2.4×10^{-2}	1.8×10^{-2}
Pb^{2+}	2.5×10^{-2}	2.0×10^{-2}
Hg^{2+}	3.0×10^{-2}	3.2×10^{-2}
Al^{3+}	3.0×10^{-2}	2.8×10^{-2}
Fe^{3+}	3.2×10^{-2}	3.0×10^{-2}

by the Fixed Interference Method (FIM), using the following expression (Nicolosky–Eisenman equation under limiting conditions):

$$K_{i,j}^{\text{Pot}} = \frac{a_i}{(a_j)^{z_i/z_j}} \quad (1)$$

Saez de Viteri and Diamond [18] have proposed a modification in the Nicolosky equation (Eq. (1)) and neglected the power term from the equation for calculating the selectivity coefficients:

$$K_{i,j}^{\text{Pot}} = \frac{a_i}{a_j} \quad (2)$$

where a_i is the activity of the primary ion and a_j is the activity of interfering ion and z_i and z_j are their respective charges. The same may also be calculated by Matched Potential Method (MPM). In the original procedure devised by Gadzekpo and Christian [19] the selectivity coefficient $K_{i,j}^{\text{Pot}}$ is given by the expression:

$$K_{i,j}^{\text{Pot}} = \frac{a'_i - a_i}{a_j} \quad (3)$$

and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_i to a'_i and a_j represents the activity of interfering ion added to same reference solution of activity a_i which brings about same potential change. In the present studies $K_{i,j}^{\text{Pot}}$ has been calculated for a range of interfering ions using the modified form of Fixed Interference Method (Eq. (2)) and Matched Potential Method (Eq. (3)). The experimental conditions, a_i (1.0×10^{-3} M Cu^{2+}), a'_i (1.0×10^{-2} M Cu^{2+}) and a_j (1.0×10^{-2} M Cu^{2+}), were taken to measure the selectivity coefficients.

A perusal of data (Table 3) clearly shows that all the ions listed will not interfere if present in lesser amounts. However, Cd^{2+} ions may cause some interference, if present in higher amount. To have an actual idea of the level of interference

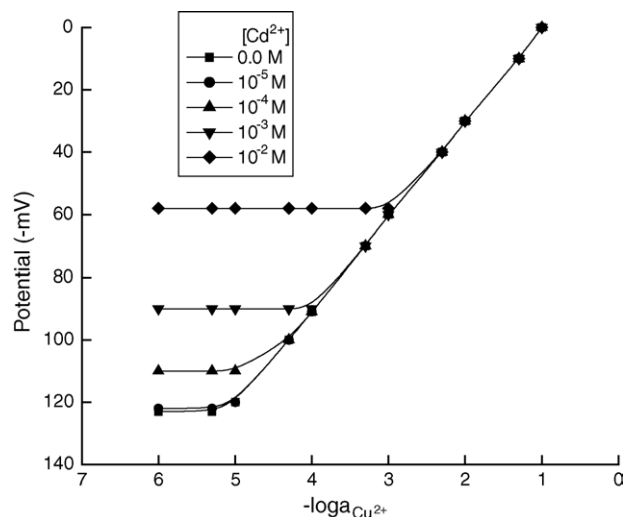


Fig. 3. Variation of membrane potential as a function of Cu^{2+} concentration in presence of different concentrations of Cd^{2+} ions.

caused by Cd^{2+} ions when present at varying concentrations, some mixed run studies [20] were performed. Fig. 3 shows that in presence of 1.0×10^{-2} , 1×10^{-3} and 1×10^{-4} M Cd^{2+} ion, the sensor can be used to determine Cu^{2+} in the reduced concentration ranges of 5.0×10^{-3} to 1.0×10^{-1} , 3.1×10^{-4} to 1.0×10^{-1} and 5.0×10^{-5} to 1.0×10^{-1} M, respectively.

3.5. Analytical applications

The electrode has been used as an indicator electrode in the titrimetric determination of copper ions. A 15 mL solution of 1.0×10^{-3} M Cu^{2+} was titrated against a 1.0×10^{-2} M EDTA solution at a constant pH of 4.0. The end point corresponds to the 1:1 stoichiometry of the Cu^{2+} :EDTA complex (Fig. 4).

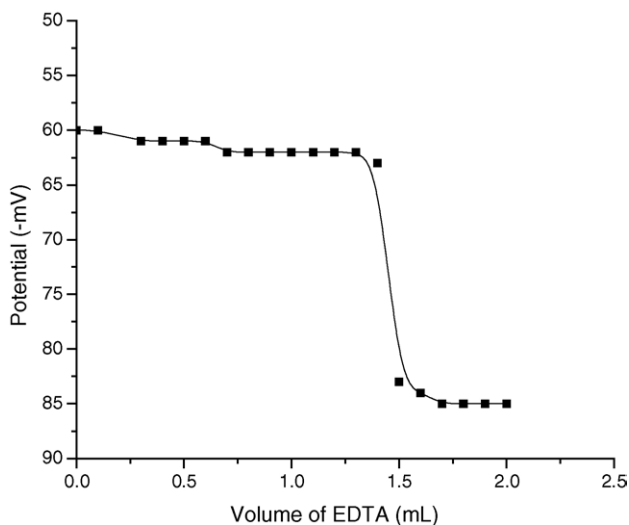


Fig. 4. Potentiometric titration curve of Cu^{2+} ions (1.0×10^{-3} , 15 mL) with EDTA (1.0×10^{-2}).

Table 4
Comparison of proposed Cu²⁺ selective electrode with reported electrodes

S. no.	Ref. no.	Detection limit (ppm)	Selectivity	Slope (mV/decade)	Response time (s)	Life time (month)
1	Jain et al. [2]	63.0	Poor	20	30	NM
2	Gupta et al. [6]	0.5	Very good	29.9	11	6
3	Yoshimoto et al. [4]	0.10	Good	29.1	10	NM
4	Gismera et al. [5]	0.63	Poor	27.2	NM	NM
5	Pleniceanu et al. [13]	3.1	Good	Nernstian	NM	NM
6	Sun et al. [11]	0.6	Good	Nernstian	NM	NM
7	Ren et al. [12]	0.3	Good	28.3	40	8 Days
8	Proposed electrode	0.5	Very good	30.0	10	>3

4. Conclusions

A comparison of proposed sensor with the reported electrodes presented in Table 4 indicates that the sensor is of comparable performance with regard to working concentration range, slope and lifetime but superior in selectivity and response time. Further the electrode was used as indicator electrode in the titrimetric determination of copper ions.

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