

Copper Incorporated [Me₂(15)dieneN₄] Macrocyclic Complex for Fabrication of PVC based Membrane Electrode for Copper

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Abstract

Copper (II) complex of 2,4-dimethyl-1,5,9,12-tetraazacyclopentadeca-1,4-diene, [Me₂(15)dieneN₄] was synthesized and used in the fabrication of Cu²⁺ – selective ISE membrane in PVC matrix. The membrane having Cu(II) macrocyclic complex as electroactive material along with sodium tetraphenyl borate (NaTPB) as anion discriminator. Dibutyl phthalate (DBP) as plasticizer in poly(vinyl chloride) (PVC) matrix was prepared for the determination of Cu²⁺. The best performance was observed by the membrane having Cu(II) complex–PVC–NaTPB–DBP with composition 1:5:1:3. The sensor worked well over a concentration range 1.12×10^{-6} M– 1.0×10^{-1} M between pH 2.1–6.2 and a fast response time 10 ± 2 s and a lifetime of 6 months. Their performance in partially non-aqueous medium was found satisfactory. Electrodes exhibited excellent selectivity for Cu²⁺ ion over other mono-, di-, trivalent cations. It can also be used as indicator electrode in the potentiometric titration of Cu²⁺ against EDTA as well as in the determination of Cu²⁺ in real samples.

Introduction

Toxicity is the utmost concern in dealing with hazardous substances. This includes the chronic copper poisoning related to haemochromatosis and produces gastrointestinal catarrch when present in large amount. It is also the fundamental cause of Wilson's disease. The potential sources of copper in industrial effluents include electrical equipments, kitchen utensils, pulp and paper mills, plating baths and the fertilizer industry. It is also essential for environmental pollution control and industrial applications [1]. The cyclam derivatives exhibit rich coordination chemistry with a variety of transition metal ions [2, 3]. Recently, few ISEs for metal ions based on their metal complexes have been reported [4–7].

Due to the vital importance of copper in biological, environmental and industrial systems and the urgent need for a highly selective and sensitive copper sensor for potentiometric determination of copper in these systems, a number of potentiometric sensors based on different ionophores have been reported [8–25]. However, most of these copper selective sensors have some or all of the following problems, high detection limit, narrow working concentration range, high response time, poor selectivity, poor reproducibility and significant interfering cations as Fe³⁺, Na⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Hg²⁺, Ag⁺ and K⁺.

The chelate complexes with bivalent metal ions like Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ of [Me₂(15)dieneN₄] were synthesized. These metal complexes of the ligands were incorporated in the membrane electrode for various metal ions. The copper (II) complex of [Me₂(15)dieneN₄] is highly selective for Cu²⁺ ion over other metal ions. The geometry of the ligand is expected to be conserved even if the metal ion is knocked out and the cavity size if the embedded chelate shall remain specific to Cu²⁺. In this paper, we report a highly selective copper electrode using copper (II) complex of [Me₂(15)dieneN₄] as a novel carrier for the potentiometric monitoring of ultra trace amounts of Cu²⁺ ion in various samples.

Experimental

Reagent and materials

All the reagents and chemicals used were of analytical grade. Acetylacetone was obtained from S.d. Fine Chem (India), N,N'-bis(3-aminopropyl)ethylenediamine from Lancaster (Germany), Sodium tetraphenylborate (NaTPB) from BDH (UK), dibutylphthalate (DBP) from Reidel (India) and dioctylphthalate (DOP) from Acros Organics (India). High molecular weight poly(vinyl chloride) PVC was obtained from Fluka (Switzerland). All the metal salts used were of analytical grade. Double distilled water was used for the prepa-

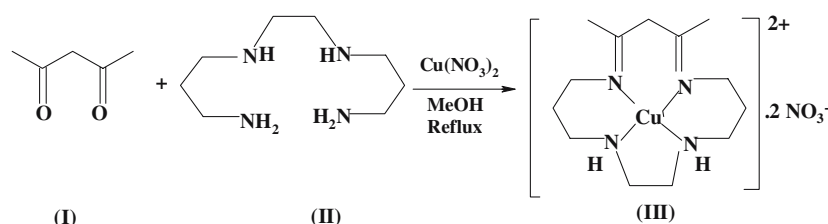
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ration of solutions of metal salts of different concentration by diluting stock standard solutions (0.1 M).

Synthesis of [Me₂(15)dieneN₄] macrocycle-Cu(II) complex(III)

Acetylacetone (I) (0.02 mol, 200 ml) dissolved in minimum quantity of dry methanol was mixed with a solution of N,N'-bis(3-aminopropyl)ethylenediamine (II) (0.02 mol, 3.48 ml) in methanol. A methanolic solution of copper nitrate (0.02 mol) was added to the mixture. The resulting mixture was refluxed 6 h and concentrated to half of its volume. The mixture was cooled at room temperature. The crystals (III) were separated out and filtered, washed with methanol and dried in vacuum (M.P. \approx 220 °C) yield 68%. [Cu (C₁₃H₂₆N₄) (NO₃)₂ – calculated (%): C, 36.66; H, 6.15; N, 19.73; Cu, 14.92 – Found (%): C, 36.62; H, 6.18; N, 19.68; Cu, 14.96]. ¹H-NMR: δ 2.16 (s, 6H) methyl protons, 2.83–3.36 (m, 16H) methylene protons, 4.32 (s, 2H) methylene protons of acetylacetone moiety and 4.62 (s, 2H) – NH protons.

The calculated and observed elemental analysis data are in good agreement with the structure: Scheme 1.



Copper (II) complex of 2,4-dimethyl-1,5,9,12-tetraazacyclopentadeca-1,4-diene (III)

Preparation of membrane

Besides the critical role of the nature of ion carrier in preparing membrane-selective sensors, some other important features of the PVC membrane, such as amount of ionophore, nature of solvent mediator, plasticizer/PVC ratio, and especially the nature of additives used, are known to significantly influence the sensitivity and selectivity [26–34]. A number of membranes were prepared with ion-active material (ionophore), an appropriate amount of PVC, solvent mediators/plasticizer and an anion discriminator (Table 1), which were dissolved in THF (20 ml). The

mixture was vigorously stirred and the air bubbles were removed. It was poured into polyacrylate rings, which were placed on a smooth glass plate and THF was allowed to evaporate slowly at room temperature. The membranes, thus obtained were detached from glass plate, and cut to suitable size and glued to one end of a 'Pyrex' glass tube with araldite.

Emf measurement

The proper equilibration of the membrane to be used as a sensor is essential for generating stable and reproducible potentials and to avoid long response time. All the membranes were immersed in Cu(NO₃)₂ solution of different concentrations for different time periods. The potential measurements were carried out at 25.0 \pm 0.1 °C by using saturated calomel electrodes (SCE) as the reference electrodes, emf measurements were carried out with the following assembly:

Internal reference electrode (SCE)/Internal solution/Membrane/Test solution/External reference electrode (SCE).

The potentials were measured by varying the concentration of the test solution in the range 1.0 \times 10⁻⁷–

1.0 \times 10⁻¹ M. To optimize the concentration of the internal solution, the potentials were measured as a function of metal ion concentration for three concentrations of internal solution, 1.0 \times 10⁻² M, 1.0 \times 10⁻¹ M and 1.0 M (Figure 1).

Dissolution of waste sample

(a) Electroplating waste

The solid electroplating waste was dried at about 120 °C overnight and 1.0 g of the waste was dissolved into 100 ml of distilled water. About 50 ml of electroplating waste was then filtered and 5 ml of

Table 1. Composition and response characteristics of Cu²⁺-selective PVC-based membrane containing [Me₂(15)dieneN₄]Cu(II) macrocyclic complex as electroactive material

Membrane no.	Composition of membrane (% w/w)					Working concentration range (M)	Slope (mV/decade of concentration)	Response time (s)
	Ionophore	PVC	NaTPB	DOP	DBP			
1	10	50	10	30	–	5.01 \times 10 ⁻⁵ –1.0 \times 10 ⁻¹	30.9	35
2	10	50	10	–	30	1.12 \times 10 ⁻⁶ –1.0 \times 10 ⁻¹	29.9	10
3	10	60	10	20	–	6.31 \times 10 ⁻⁵ –1.0 \times 10 ⁻¹	28.4	25
4	10	60	10	–	20	8.91 \times 10 ⁻⁶ –1.0 \times 10 ⁻¹	28.2	20

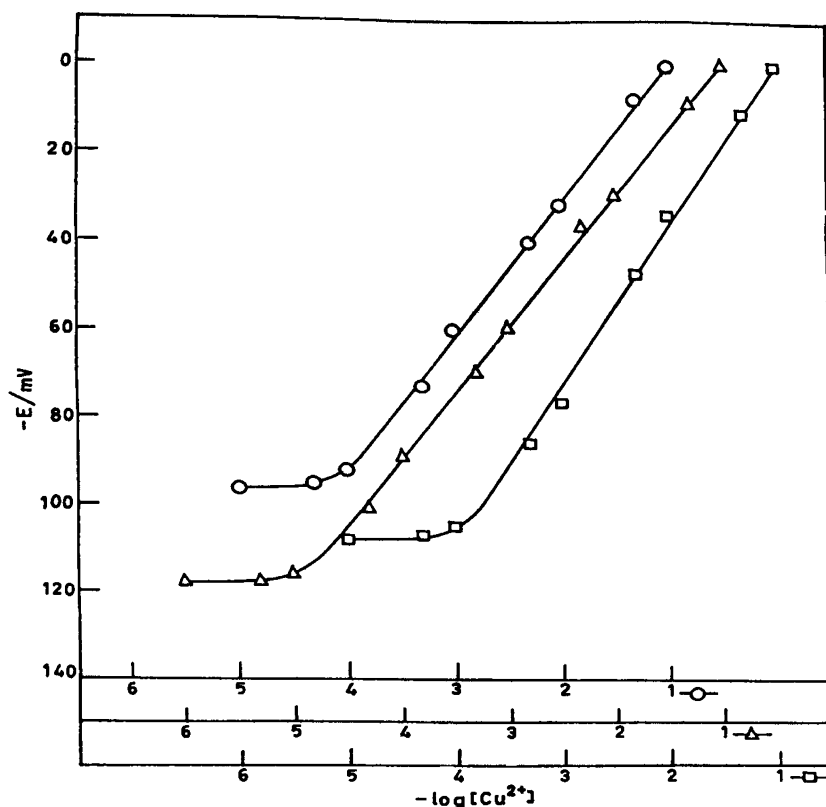


Figure 1. Plots showing the variation of the cell potentials with Cu^{2+} concentration at three concentrations of internal solutions 1.0×10^{-2} M (○), 1.0×10^{-1} M (Δ) and 1.0 M (□).

conc. H_2SO_4 was added to it. The final volume of solution was made up to 60 ml maintaining the pH between 3.0 and 4.0. The solution was suitably diluted for determination of metal concentration by AAS.

(b) Spent Fe–Cr catalyst

The solid spent Fe–Cr catalyst was dried at about 110°C overnight before dissolution. One gram of spent Fe–Cr catalyst was heated with 10 ml portions of conc. HCl and further repeated twice to near dryness. The residue was dissolved in 10 ml of 0.1 M H_2SO_4 and made up to 100 ml and pH was maintained at 4.0.

All the solutions were suitably diluted and metal concentrations were determined with AAS.

Results and discussion

Membranes of $[\text{Me}_2(15)\text{dieneN}_4]$ copper(II) complex were prepared by dissolving the ionophore and PVC in THF. The ratio of ionophore to PVC was varied in order to obtain the composition, which gives the membrane having best performance with regard to working concentration range, slope and response time. It was found that the membrane having the ionophore, PVC and anion excluder (NaTPB) in the ratio 1:5:1(w/w) gives the best performance. The effect of anion discriminator [35–38] and plasticizer (solvent mediator),

which are used frequently to improve electrochemical properties of PVC membranes were also studied. For this purpose solvent mediators *viz.* dibutylphthalate (DBP) and dioctylphthalate (DOP) were tried. Membranes having different ratios of ionophore, PVC, NaTPB, DBP and DOP were prepared. The composition of the membranes showing the best results is given in Table 1.

The membranes were equilibrated with 1.0 M copper nitrate solution before starting any potential studies. It was found that equilibrated membranes gave reproducible results and no drift in potentials was observed after 3 days of equilibration. The potentials of different membrane electrode as a function of copper nitrate concentration were plotted in Figure 2. The concentration range over which the electrodes give almost linear potential response is taken as their working concentration range. The working concentration range for different electrodes as evaluated from Figure 2, are given in Table 1. It can be seen from Table 1, on addition of anion discriminator and plasticizer to the membranes (electrode nos. 1–4), the membranes incorporating solvent mediators DOP (electrode no. 1), DBP (electrode no. 2) and varying ratio of DOP (electrode no. 3) and DBP (electrode no. 4) along with anion discriminator, NaTPB exhibited linearity in the concentration range 5.01×10^{-5} – 1.0×10^{-1} , 1.12×10^{-6} – 1.0×10^{-1} , 6.31×10^{-5} – 1.0×10^{-1} and 8.91×10^{-6} – 1.0×10^{-1} M with slopes 30.9 ± 0.4 , 29.9 ± 0.3 , 28.4 ± 0.4 and 28.2 ± 0.4 mV per decade of activity, respectively. It

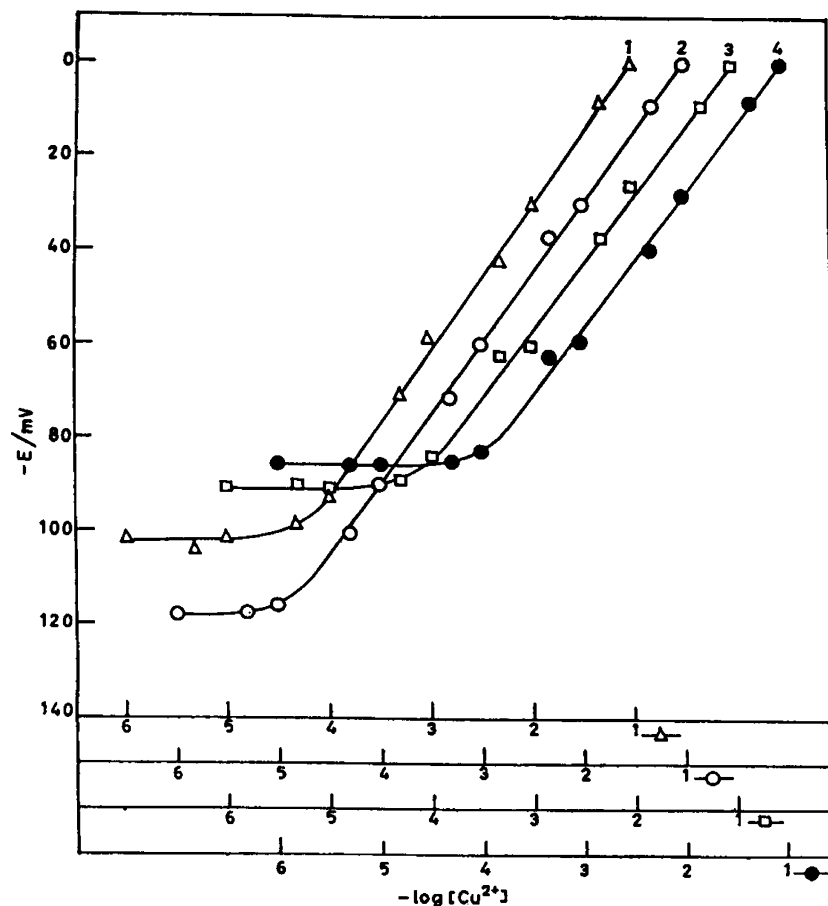


Figure 2. Plots showing the variation of membrane potentials with the concentration of Cu^{2+} ions.

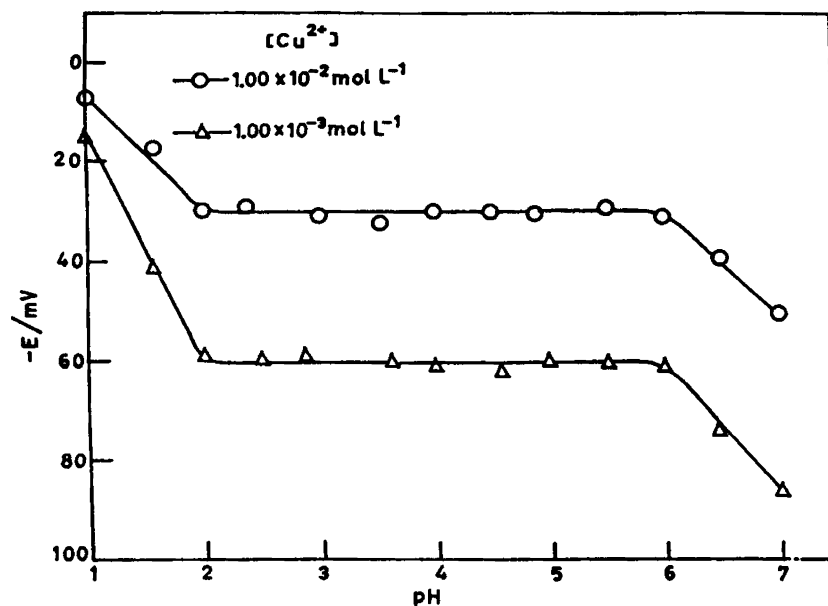


Figure 3. Plots showing the variation of membrane potentials with pH at 1.0×10^{-2} M and 1.0×10^{-3} M Cu^{2+} solutions.

can, thus, be inferred that the membrane no. 2, incorporating ionophore, DBP as the solvent mediator, NaTPB as anion discriminator and PVC in the ratio 1:5:1:3 gives the best performance with regard to working concentration range and slope as compared to

the rest of the membranes. This membrane gave standard deviation of ± 0.5 mV in observed values of potentials from the least square fit line with very good consistency in slope with 90% confidence limit lying within ± 0.3 mV per decade of activity. Repeated

Table 2. Selectivity coefficient values for Cu (II) ion-selective membrane electrode for sensor no. 2

Interfering ion (B)	Selectivity coefficients by matched potential method (at 1.00×10^{-2} M concentration of interfering ions)
NH_4^+	2.04×10^{-1}
K (I)	1.87×10^{-1}
Na (I)	2.22×10^{-1}
Ag (I)	1.68×10^{-1}
Mg (II)	6.24×10^{-2}
Cd (II)	3.60×10^{-2}
Ba (II)	1.99×10^{-2}
Co (II)	3.26×10^{-1}
Mn (II)	3.10×10^{-1}
Hg (II)	1.00×10^{-2}
Ni (II)	4.22×10^{-1}
Pb (II)	8.12×10^{-2}
Zn (II)	2.29×10^{-1}
Fe (III)	7.80×10^{-3}
Al (III)	4.40×10^{-3}
Cr (III)	2.00×10^{-3}

monitoring of potentials (15 measurements) on the same portion of the sample gave reproducibility in results with a maximum of about 1% error.

The response time has been measured as the time taken by the electrode to attain a stable potential. It was

determined for all membranes (Table 1). Though the response times of membranes with DOP and DBP were 35, 10, 25 and 20 s, respectively. The best response time (10 s) was shown by membrane no. 2, incorporating DBP as solvent mediator. The potentials remained stable and constant for more than 5 min. This sensor could be successfully used over a period of more than 6 months at a stretch without any significant change in working concentration range, slope and response time. After this period a drift in potentials was observed which could be corrected by reequilibrating the membrane with 1.0 M Cu^{2+} solution for 2–3 days. The sensor was kept in 0.1 M Cu^{2+} solution when not in use.

The pH dependence of the electrode potentials was tested at 1.0×10^{-2} M and 1.0×10^{-3} M Cu^{2+} solution by varying the pH in the range 1.0–7.0. The potentials remained constant in the pH range 2.1–6.2 (Figure 3) and the same may be taken as the working pH range of the sensor. The sharp changes in potential below pH 2.1 may be ascribed to H^+ co-fluxing and above pH 6.2 may be due to the hydrolysis of Cu^{2+} ions.

The functioning of the sensor was also tested in partially non-aqueous media using methanol–water and ethanol–water mixtures. It was observed that the sensor could tolerate up to 35% (v/v) non-aqueous content. The working concentration range reduced sharply, but the slope remained unaffected when the non-aqueous content exceeds this limit.

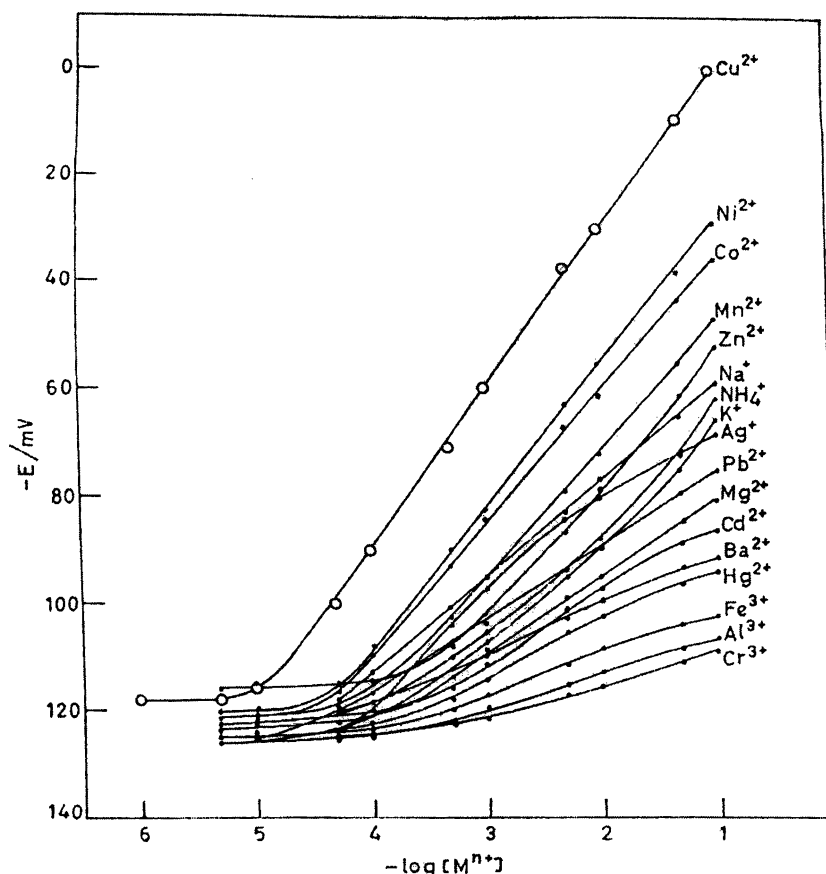


Figure 4. Potential response of ion-selective electrode with $[\text{Me}_2(15)\text{dieneN}_4]$ Copper (II) complex as ionophore for various metal ions.

Table 3. Analytical data for electroplating waste and spent iron–chromium catalyst waste as determined by AAS and Cu²⁺ sensor no. 2

S. no.	Spent iron–chromium catalyst waste		Electroplating waste	
	Concentration of Cu(II) as determined by AAS (mg g ⁻¹)	Concentration of Cu (II) as determined by the proposed Cu(II) sensor (mg g ⁻¹)	Concentration of Cu(II) as determined by AAS (mg g ⁻¹)	Concentration of Cu(II) as determined by the proposed Cu(II) sensor (mg g ⁻¹)
1	2.55 ± 0.01	2.53 ± 0.03	7.85 ± 0.01	7.80 ± 0.03
2	2.60 ± 0.01	2.56 ± 0.03	7.80 ± 0.01	7.75 ± 0.03
3	2.65 ± 0.01	2.63 ± 0.03	7.88 ± 0.01	7.85 ± 0.03
4	2.67 ± 0.01	2.60 ± 0.03	7.90 ± 0.01	7.85 ± 0.03

Table 4. Comparison of the proposed Cu²⁺-selective electrode with the reported electrode

Sensor	Working concentration range (M)	Slope/mV (decade activity) ⁻¹	pH range	Response time (s)	Life time (months)	Selectivity	Reference
1	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻¹	NM	NM	NM	NM	NM	[5]
2	8.0 × 10 ⁻⁵ –1.0 × 10 ⁻²	NM	NM	NM	NM	NM	[6]
3	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻¹	Near Nernstian	1.9 – 5.2	NM	NM	Sufficiently selective	[7]
4	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻¹	Nernstian	NM	NM	NM	Highly selective	[8]
5	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻²	Nernstian	5.0 – 8.0	15	5	Sufficiently selective	[9]
6	5.0 × 10 ⁻⁵ –5.0 × 10 ⁻¹	Nernstian	NM	NM	NM	Highly selective	[13]
7	2.5 × 10 ⁻⁵ –1.0 × 10 ⁻¹	Near Nernstian	2.1 – 5.5	13	5	Highly selective	[14]
8	8 × 10 ⁻⁶ –1.0 × 10 ⁻¹	Nernstian	3.0 – 6.5	15	3	Sufficiently selective	[15]
9	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻¹	Nernstian	3.5 – 6.5	10	2	Sufficiently selective	[19]
10	1.12 × 10 ⁻⁶ –1.0 × 10 ⁻¹	Nernstian	2.1 – 6.2	10	6	Highly selective	Proposed sensor

The selectivity coefficient values evaluated by Matched potential method [39] Table 2. Figure 4 clearly indicates that the electrode is highly selective to Cu²⁺ ion over various monovalent, divalent and trivalent cations. Although, Na⁺, Co²⁺, Ni²⁺ are likely to cause some interference as the selectivity coefficient values are higher for these ions, but they may also not cause any interference at low concentration, as selectivity is concentration dependent. The electrode can tolerate Na⁺ up to concentrations ≤5.0 × 10⁻⁵ M, Co²⁺ up to concentrations ≤6.5 × 10⁻⁵ M and Ni²⁺ up to concentrations ≤5.5 × 10⁻⁵ M, respectively over the entire working concentration range.

The proposed Cu²⁺ membrane electrode was found to work well under laboratory conditions. It was successfully applied to the potentiometric titration of Cu²⁺ ions against EDTA. 10 ml solution of 1.0 × 10⁻² M Cu²⁺ was titrated against 1.0 × 10⁻² M EDTA at pH 4.0. The conventional sigmoid shaped plot is not obtained which may be due to the electrode's response to the Na⁺ ions of the disodium EDTA salt. However, the endpoint corresponds to the stoichiometry of Cu–EDTA complex.

The electrode was applied for the determination of Cu²⁺ ions in electroplating waste sample and spent iron–chromium catalyst waste. The results obtained were in good agreement with those obtained from AAS (Table 3) and the sensor can be successfully employed for the determination of Cu²⁺ in real samples.

Conclusions

A comparative data of the proposed Cu²⁺ sensor along with those reported in the literature is summarized in Table 4. It can be clearly seen from the table that the present studies have helped in developing a better sensor than the existing sensors for Cu²⁺ in terms of working concentration range, pH range, response time, life time and application to real sample analysis.

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