Cu(II) selective sensor based on 5,7,12,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraaza-cyclotetradecane in PVC matrix

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Abstract

5,7,12,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecane, $Me_4Bzo_2[14]aneN_4$. (**I**) was synthesized and used as an electroactive material for the fabrication of membrane electrode in PVC matrix for the determination of Cu^{2+}. The best performance was given by the membranes of macrocycle (**I**) with composition 5:3:100:150 (**I**: NaTPB:DBBP:PVC). The sensor worked well over a concentration range 2.5×10^{-5}–1.0×10^{-1} M of Cu^{2+} with a slope of 30.2 ± 0.3 mV $(decade)^{-1}$ of Cu^{2+} activity, a fast response time of 13 ± 2 s and a lifetime of five months. The working pH range of this sensor is 2.6–5.5 and it shows excellent selectivity for Cu^{2+} over other mono-, di- and trivalent cations. Its performance in partially nonaqueous medium was found to be satisfactory. The sensor can also be used as an indicator electrode in the potentiometric titration of Cu^{2+} against EDTA and its determination in real samples.

1. Introduction

Potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production and the fertilizer industry. Copper is also present in some sea weeds and certain invertebrates. The maximum contaminant level (MCL) for copper is 1.0 mg L^{-1} [1] and its excessive intake results in accumulation in liver. Chronic copper poisoning is related to haemochromatosis and produces gastrointestinal catarrh when present in large amounts. Copper toxicity is also a fundamental cause of Wilson's disease. The monitoring of copper is, therefore, essential for environmental pollution control and industrial applications.

The cyclam derivatives exhibit rich coordination chemistry with a variety of transition metal ions. This has been extensively exploited in synthesizing a variety of thermodynamically stable N_4 macrocycle amine complexes with varying ring sizes [2, 3] and many saturated macrocycles have been used for the fabrication of ion-selective membrane electrodes for copper ion detection. The 14-membered dibenzocyclam has particularly been found to give a more selective potentiometric sensor. However, the polymeric matrix, the steric and conformational requirements of saturated 14-membered dibenzocyclam impedes the facile interaction of the metal ion. Therefore, the ion-selective electrodes reported for the determination of Cu^{2+} in the literature to date exhibit poor selectivity, a narrow concentration range, non-Nernstian response, long response time and poor reproducibility [4–16]. In this paper, results on a PVC matrix membrane sensor incorporating $Me_4Bzo_2[14]aneN_4$ macrocycle (**I**) as ionophore for the determination of copper in aqueous solutions are presented and discussed.

2. Experimental details

2.1. Reagents and materials

All reagents used in the investigations were of Analytical Grade (BDH, UK). Nickel acetate from Veb lab (Germany); acetylacetone from Sigma (USA) and *o*-phenylenediamine, and 1-butanol from Loba Chemie (India) were used. Spectroscopic grade methanol and chloroform were used for electronic spectral studies. Different solvent mediators/plasticizers such as chloronaphthalene (CN), and tris(2-ethylhexyl) phosphate (TEP) were obtained from Merck (Germany), dibutyl butylphosphonate (DBBP), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) from Reidel (India). High molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka (Switzerland) and sodium tetraphenyl borate (NaTPB) from BDH (UK) and used as such. AR grade tetrahydrofuran (THF), nitric acid and sulfuric acid were obtained from E. Merck (India) and sodium hydroxide from Ranbaxy (India). All the metal salts used were of analytical reagent grade. Solutions of metal

nitrates were prepared in doubly distilled water and standardized by appropriate chemical methods.

2.2. Synthesis of Me$_4$Bzo$_2$[14]aneN$_4$ macrocycle (I)

The metal-free dibenzocyclam (I) was synthesized and characterized using the reported method [17]. A mixture of [Ni(Me$_4$Bzo$_2$[14]aneN$_4$]Cl$_2$ (II) (1.2 g, ~2.5 mmol) and NaCN (1.0 g, ~20.4 mmol) in H$_2$O (50 cm^3) was refluxed for 5 h. It was cooled to room temperature, and then NaOH (0.5 g) was added. The resulting suspension was subsequently evaporated to near dryness on a rotatory evaporator. The viscous semi-solid mass was extracted with five portions of CHCl$_3$ (10 cm^3). The CHCl$_3$ extracts were combined and evaporated to dryness. The solid residue was purified by passing it through a 10×2.5 cm neutral Al$_2$O$_3$ column eluting with CHCl$_3$. The main yellow band moved fairly rapidly. It was collected and solvent was removed at reduced pressure. The crude product was recrystallized from benzene/petroleum ether to give yellowish brown coloured crystals. Yield: 0.5 g (57%).

The metal-free macrocycle (I) is soluble in less polar organic solvents like CHCl$_3$ and benzene, and undergoes slow aerial oxidation in the dry state. However, this macrocycle remains stable in aqueous solutions and no oxidation was observed. The mass spectral data of macrocycle (I) is in agreement with the proposed structure giving molecular ion peak at m/z 352. The IR spectra of the metal-free macrocycle (I) exhibits a medium intensity band at 1269 cm^{-1} [v_{str}(C—N)] and phenyl ring bands at 1450 cm^{-1} and 1405 cm^{-1} [v_{str}(C=C)] and is indicative of a saturated macrocycle framework. The metal-free macrocycle (I) exhibits ^{1}H NMR signals at around δ 7.0 H(Ar), 3.74 (CH), 1.87 (CH$_2$) and 4.5 p.p.m. (NH). Macrocycle (I) gave bands at λ_{max} 273 nm (ε_{max} 30 000 m^{-1} cm^{-1}) and 247 nm (ε_{max} 28 000 m^{-1} cm^{-1}).

(I)   (II)
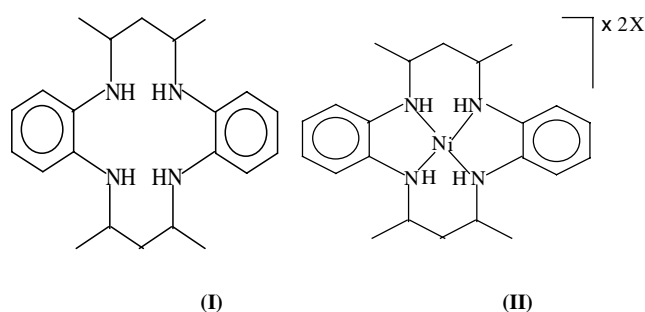
2.3. Preparation of membranes

A number of membranes incorporating the ionophore, anion excluder and plasticizers in different ratios in PVC matrix were fabricated by the Craggs method [18]. Varying amount of ion-active material (~3.0–20 mg) and an appropriate amount of PVC (~50–200 mg) were dissolved in ~20 mL tetrahydrofuran (THF). Anion excluder NaTPB (~1.0–10 mg) and solvent mediators, DBBP, DBP, TEP, CN, DOP (~50–250 mg) were also added to get membranes of different compositions. The mixture was vigorously shaken and the air bubbles were removed. It was poured into polyacrylate rings, placed on a smooth glass plate, and THF was allowed to evaporate at room temperature. The membranes, so obtained, were detached from the glass plate, cut to suitable size and glued to one end of a 'Pyrex' glass tube with araldite.

2.4. Equilibration of membranes and potential measurements

Proper equilibration of a membrane is essential to get stable and reproducible potentials and avoid long response time. It is necessary to optimize the concentration of the contacting solution and the time required for complete equilibration. Thus, all the membranes were immersed in respective metal salt solutions of different concentrations for different time periods.

The potential measurements of the following cell assembly set-up using saturated calomel electrodes (SCE) as references were carried out at 25 ± 0.1 °C:

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 1.0×10^{-6}–1.0×10^{-1} M. To optimize the concentration of the internal solution, potentials were measured at three concentrations of internal solution, namely 1.0×10^{-2}, 5.0×10^{-2} and 1.0×10^{-1} M.

2.5. Dissolution of waste samples

2.5.1. Treatment of electroplating waste
The solid electroplating waste was dried at about 110 °C overnight and 1.0 g of the waste was dissolved into 100 mL of distilled water. The average content of the electroplating waste was 21% Cr, 10% Ni, 4.2% Cu, 0.83% Fe, 0.52% Pb, 0.98% Zn, 0.24% Al and 0.13% Mn (% by weight) and the pH of the waste solution was around 3.0. 40 mL of electroplating waste solution was then filtered and 5 mL of concentrated sulphuric acid was added to it. The final volume of solution was made up to 50 mL maintaining the pH between 3.0–4.0 and suitably diluted further for AAS measurements.

2.5.2. Dissolution of spent Fe–Cr catalyst
The solid spent Fe–Cr catalyst was dried at about 100 °C overnight before dissolution. The waste had 0.37% Cr, 0.29% Ni, 0.21% Cu, 0.23% Fe and 0.05% Zn (% by weight). 1.0 g of spent Fe–Cr catalyst was heated with two 10 mL portions of concentrated HCl to near dryness. The residue was dissolved in 10 mL of 0.1 M H$_2$SO$_4$ and made up to 100 mL. The pH of the solution was maintained at 4.0.

3. Result and discussion

The composition of PVC-based membranes of 5,7,12, 14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecane (**I**) was optimized by varying the ratio of the macrocycle (**I**) and PVC so as to achieve a membrane that shows satisfactory performance with regard to working concentration range, slope and response time. It was found that the membrane incorporating macrocycle (**I**), anion discriminator (NaTPB) and PVC in the ratio 5:3:150 (w/w) gives the best response. Experiments concerning equilibration of membranes showed that appropriate equilibration was achieved when these were dipped in 1.0 M Cu^{2+} for three days. No drift in potential was observed with these membranes.

In view of the fact that the selectivities and sensitivities obtained for a given membrane depend significantly on its composition, different ratios of anion discriminator, sodium tetraphenyl borate (NaTPB) and solvent mediator such as dibutyl butylphosphonate (DBBP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), chloronaphthalene (CN) and tris(2-ethyl-hexyl)phosphate (TEP) were tried. The composition of the membranes which gave best results are given in Table 1.

3.1. Working concentration range and slope

The potential response of the membranes as a function of Cu^{2+} activity is given in Table 1. It is seen that membrane 1 without plasticizer exhibits a narrow working concentration range of 3.16×10^{-4}–1.0×10^{-1} M with nonnernstian slope of 37.0 ± 0.8 mV (decade)$^{-1}$ of activity (Table 1). Among five different plasticizers, the membranes with DBBP gives the best performance with regard to working concentration range, slope and response time. Membrane 2 exhibited a working concentration range of 2.5×10^{-5}–1.0×10^{-1} M with a nearnernstian slope of 30.2 ± 0.3 mV (decade)$^{-1}$. Membrane 3 with DBP as solvent mediator exhibited a working concentration range of 1.58×10^{-4}–1.0×10^{-1} M with a slope of 35.2 ± 0.6 mV (decade)$^{-1}$ while membrane 4 with CN showed linearity in the concentration range 6.30×10^{-5}–1.0×10^{-1} M with a slope of 34.9 ± 0.6 mV (decade)$^{-1}$. Membrane 5 containing TEP as plasticizer showed a working concentration range of 7.94×10^{-5}–1.0×10^{-1} M with a slope of 36.5 ± 0.7 mV (decade)$^{-1}$ and membrane 6 with DOP exhibited a working concentration range of 9.0×10^{-5}–1.0×10^{-1} M with a slope of 35.2 ± 0.7 mV (decade)$^{-1}$. Hence the best composition of the membrane was found to be 5:3:100:150 (**I**:NaTPB:DBBP:PVC). Membrane 2 was chosen for further studies.

The slopes of the least square fit line and standard deviation in the observed values of potential from this line are given in Table 1. Membrane 2 gives standard deviation of 2.15 mV in observed values of potential from the least square fit line. This membrane gives excellent consistency in slope with 90% confidence limit lying within ± 0.3 mV (decade)$^{-1}$. Repeated monitoring

Table 1. Compositions and characteristics of PVC based membranes having 5,7,12,14-tetramethyldibenzo-[b,i]1,4,8,11-tetraazaannulene (I) as electroactive material

Sensor	Composition of the membrane /%w/w								Working concentration range /M	Slope with 90% confidence limit /mV (decade of activity)$^{-1}$	Response time (± 2) /s	Standard deviation in potential /mV
	(I)	NaTPB	DBBP	DBP	CN	TEP	DOP	PVC				
1	5.0	2.5	–	–	–	–	–	150	3.16×10^{-4}–1.0×10^{-1}	37.0 ± 0.8	45	2.98
2	5.0	3.0	100	–	–	–	–	150	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	13	2.15
3	5.0	3.0	–	150	–	–	–	150	1.58×10^{-4}–1.0×10^{-1}	35.2 ± 0.6	29	3.48
4	5.0	3.0	–	–	200	–	–	150	6.30×10^{-5}–1.0×10^{-1}	34.9 ± 0.6	25	3.26
5	5.0	3.0	–	–	–	200	–	150	7.94×10^{-5}–1.0×10^{-1}	36.5 ± 0.7	32	4.14
6	5.0	2.5	–	–	–	–	200	150	9.0×10^{-5}–1.0×10^{-1}	35.2 ± 0.7	25	4.01

of potentials (20 measurements) on the same portion of the sample gave reproducibility in results with a maximum of about 1% error.

3.2. Response and life time

The response time was determined for all membranes. It is seen from Table 1 that membrane 1 (without plasticizers) exhibited a response time of about 45 s while those incorporating the solvent mediators DBBP, DBP, CN, TEP or DOP (membranes 2–6), respectively, exhibited faster response time of 13, 29, 25, 32 and 25 s. The best response time is given by membrane 2 incorporating DBBP as the solvent mediator. It is important to mention here that the response time of the sensor does not change when the analyte is changed from high to low concentration. The sensor has a lifetime of more than five months, during which it could be used without any measurable divergence in potentials. The time of contact and concentration of the equilibrating solution was also optimized so that the sensor generated stable and reproducible potentials at relatively short response time. It was found that an equilibrating solution of 0.5 M and contact time of three days were appropriate for smooth functioning of the electrode. Membranes were stored in 0.1 M $Cu(NO_3)_2$ solution, when not in use.

3.3. pH and solvent effect

The effect of pH on the potential of the electrode was investigated at Cu^{2+} concentration of 1.0×10^{-2} and 1.0×10^{-3} M Cu^{2+} and is shown in Figure 1. The pH was adjusted using hydrochloric acid or sodium hydroxide. From this figure, it is seen that the potential remains constant over the pH range 2.6–5.5 and same can be taken as working pH range of the sensor. It is pertinent to mention that the N atoms of the ligand remain unprotonated in this pH range because of metal
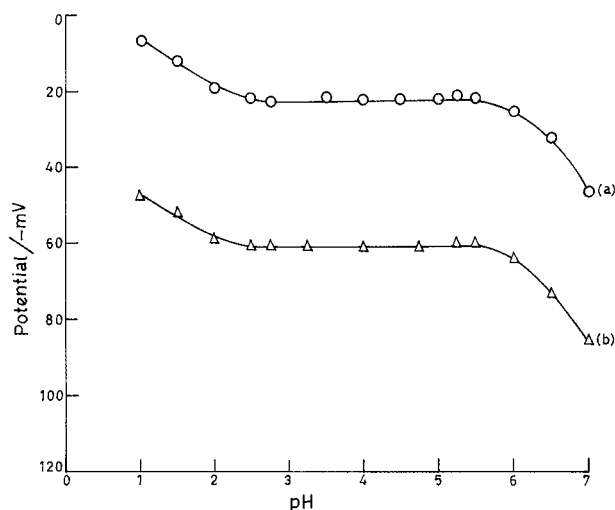

Fig. 1. Effect of pH on cell potential; $[Cu^{2+}] = 1.0 \times 10^{-2}$ M (a) and 1.0×10^{-3} M (b) for sensor 2.

Table 2. Performance of sensor 2 in partially nonaqueous media

Nonaqueous content /% v/v	Working concentration range /M	Slope with 90% confidence limit /mV (decade of activity)$^{-1}$	Standard deviation in potential /mV
0	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
Methanol			
10	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
20	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
30	2.82×10^{-5}–1.0×10^{-1}	29.5 ± 0.3	2.15
35	7.94×10^{-5}–1.0×10^{-1}	25.8 ± 0.3	2.15
Ethanol			
10	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
20	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
30	2.82×10^{-5}–1.0×10^{-1}	29.0 ± 0.3	2.15
35	8.91×10^{-5}–1.0×10^{-1}	24.2 ± 0.3	2.15
Acetone			
10	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
20	2.51×10^{-5}–1.0×10^{-1}	30.2 ± 0.3	2.15
30	3.16×10^{-5}–1.0×10^{-1}	29.5 ± 0.3	2.15
35	1.0×10^{-4}–1.0×10^{-1}	26.6 ± 0.3	2.15

coordination. The sharp changes in potential below pH 2.6 may be ascribed to H^+ co-fluxing and above pH 5.5 may be due to hydrolysis of Cu^{2+}.

The functioning of the sensor (membrane 2) was also tested in partially nonaqueous medium using methanol, acetone, and ethanol and the results obtained are compiled in Table 2. No considerable change in the value of slope or working concentration range was observed in solutions having up to 30% (v/v) nonaqueous content. Above this, the potentials generated show a continuous drift with time. It is worth mentioning that the lifetime of the membrane did not alter in nonaqueous solutions.

3.4. Potentiometric selectivity

The selectivity coefficients were evaluated by the modified form of fixed interference method as suggested by Sa'ez de Viteri and Diamond [19] and also by matched potential method [20] at 1.0×10^{-2} M interfering ion concentration. The values of selectivity coefficients $K^{Pot}_{Cu^{2+},B}$ are given in Table 3. The values indicate that the electrode is moderately selective to Cu^{2+} over a number of other cations except for Na^+ and Ni^{2+}. At lower concentrations Na^+ and Ni^{2+} would also not interfere, but may start interfering at some higher concentrations. To obtain the tolerance level of these interferents, some mixed run studies were carried out [21]. It can be seen from Figure 2 that Na^+ at $\leqslant 5.0 \times 10^{-5}$ M causes no deviation in the original plot (as obtained in pure Cu^{2+} solutions for electrode 2) and thus can tolerate $\leqslant 5.0 \times 10^{-5}$ M Na^+ over the entire working concentration range. The electrode assembly can be used to determine Cu^{2+} in the reduced concentration ranges of 6.8×10^{-5}–1.0×10^{-1}, 3.54×10^{-4}–1.0×10^{-1}, 8.91×10^{-4}–1.0×10^{-1} M at 1.0×10^{-4}, 1.0×10^{-3} and 1.0×10^{-2} M Na^+, respectively. Similarly it can be seen from Figure 3 that Ni^{2+} can be

Table 3. Selectivity coefficient values $K_{Cu^{2+}, B}^{Pot}$ for sensor 2 as obtained by modified fixed interference method and also by the matched potential method

Interfering ion (B)	Selectivity coefficient values $K_{Cu^{2+}, B}^{Pot}$	
	Fixed interference method	Matched potential method
Li^+	1.9×10^{-2}	0.14
Na^+	7.0×10^{-1}	0.71
K^+	5.0×10^{-2}	0.31
NH_4^+	1.8×10^{-2}	0.21
Tl^+	3.0×10^{-2}	0.18
Ag^+	1.1×10^{-2}	0.14
Cs^+	1.5×10^{-2}	0.13
Ca^{2+}	1.4×10^{-3}	0.17
Mg^{2+}	2.1×10^{-3}	0.21
Ba^{2+}	3.0×10^{-3}	0.14
Sr^{2+}	2.8×10^{-3}	0.14
Ni^{2+}	9.0×10^{-2}	0.67
Cd^{2+}	1.7×10^{-3}	0.10
Co^{2+}	4.7×10^{-3}	0.13
Pb^{2+}	3.9×10^{-3}	0.14
Hg^{2+}	6.8×10^{-3}	0.17
Zn^{2+}	5.6×10^{-3}	0.21
Al^{3+}	4.7×10^{-3}	0.18
Fe^{3+}	1.0×10^{-3}	0.17
Bi^{3+}	1.8×10^{-3}	0.14
Cr^{3+}	3.4×10^{-3}	0.13
Ce^{3+}	3.9×10^{-3}	0.11

tolerated over the entire concentration range if present at concentrations $\leqslant 5.0 \times 10^{-5}$ M. In the presence of 1.0×10^{-4}, 1.0×10^{-3} and 1.0×10^{-2} M Ni^{2+}, the proposed sensor can be used to determine Cu^{2+} in the reduced concentration ranges of 5.6×10^{-5}–1.0×10^{-1}, 2.98×10^{-4}–1.0×10^{-1}, 9.44×10^{-4}–1.0×10^{-1} M Cu^{2+}, respectively.
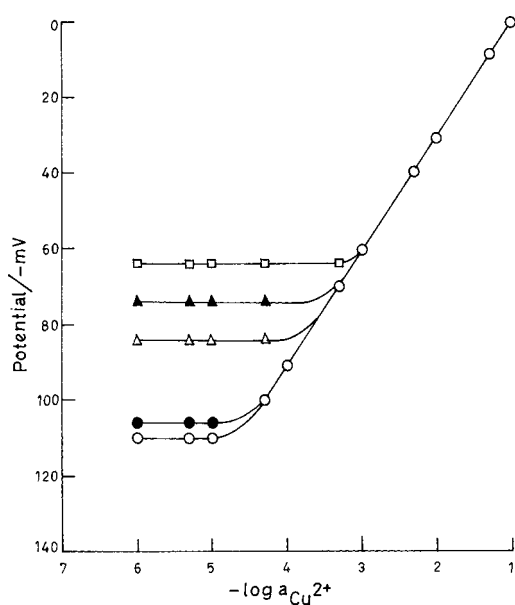

Fig. 2. Variation of cell potential with Cu^{2+} concentration at different concentration levels of Na^+ (sensor 2). Key for $[Na^+]$: (□) 1.0×10^{-2}, (▲) 1.0×10^{-3}, (△) 1.0×10^{-4} and (●) 5.0×10^{-5} M.
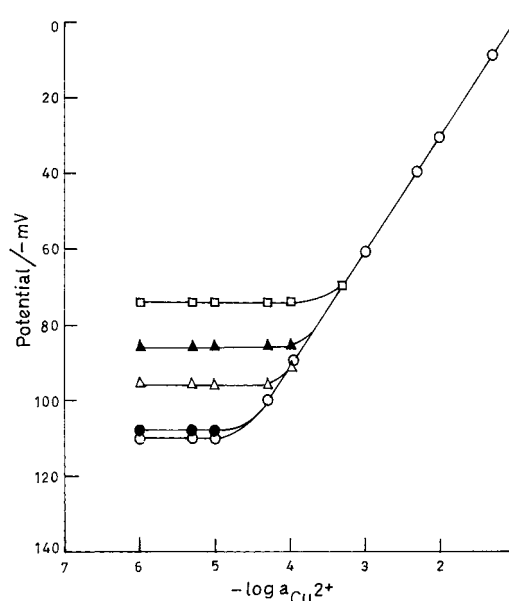

Fig. 3. Variation of cell potential with Cu^{2+} concentration at different concentration levels of Ni^{2+} (sensor 2). Key for $[Na^{2+}]$: (□) 1.0×10^{-2}, (▲) 1.0×10^{-3}, (△) 1.0×10^{-4} and (●) 5.0×10^{-5} M.

3.5. Analytical applications

3.5.1. Potentiometric titration
The proposed Cu^{2+} membrane electrode was found to work well under laboratory conditions. It was successfully applied to the potentiometric titration of Cu^{2+} against EDTA. 10 mL (1×10^{-3} M) solution of Cu^{2+} was titrated with 1×10^{-2} M EDTA at a pH 4.0 (Figure 4). The plot obtained is not of sigmoidal shape probably due to slight interference caused by Na^+ present with EDTA. However, the endpoint corresponds to the stoichiometry of Cu-EDTA complex.

3.5.2. Waste analysis
The electrode was applied for the determination of Cu^{2+} in an electroplating waste and spent iron–chromium catalyst. The results obtained were compared with those obtained from atomic absorption spectrophotometry (AAS) (Table 4). It is seen that the agreement is
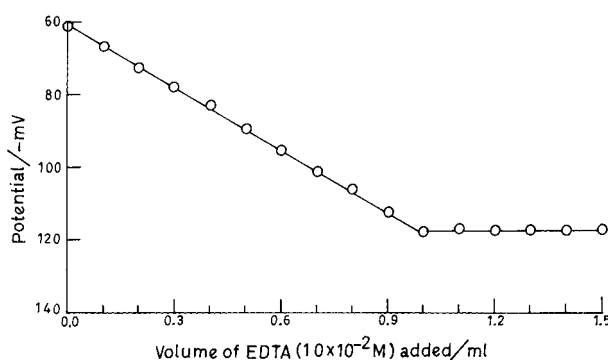

Fig. 4. Potentiometric titration of Cu^{2+} (1.0×10^{-3} M) with EDTA (1.0×10^{-2} M) (sensor 2).

Table 4. Analytical data for spent iron–chromium catalyst waste and electroplating waste as determined by AAS and Cu^{2+} sensor 2

Sl. 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	2.05 ± 0.01	2.05 ± 0.03	8.20 ± 0.01	8.15 ± 0.03
2	2.07 ± 0.01	2.00 ± 0.03	8.25 ± 0.01	8.20 ± 0.03
3	2.05 ± 0.01	1.98 ± 0.03	8.20 ± 0.01	8.10 ± 0.03

Table 5. Comparison of the proposed Cu^{2+}-selective electrode with the reported electrodes
NM not mentioned

Sensor	Working concentration range /M	Slope /mV (decade of 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	[7]
2	8.0×10^{-5}–1.0×10^{-2}	NM	NM	NM	NM	NM	[8]
3	1.0×10^{-5}–1.0×10^{-1}	near nernstian	1.9–5.2	NM	NM	sufficiently selective	[9]
5	1.0×10^{-5}–1.0×10^{-1}	nernstian	NM	NM	NM	highly selective	[10]
6	1.0×10^{-5}–1.0×10^{-2}	nernstian	5.0–8.0	15	5	sufficiently selective	[11]
7	5.0×10^{-6}–5.0×10^{-2}	nernstian	4.0–7.0	5	3	sufficiently selective	[12]
8	5.0×10^{-5}–5.0×10^{-1}	nernstian	NM	NM	NM	highly selective	[16]
9	2.5×10^{-6}–1.0×10^{-1}	near nernstian	2.1–5.5	13	5	highly selective	proposed sensor

good and therefore the membrane electrode may be used for Cu^{2+} determination in real samples.

4. Conclusion

Comparative data for the proposed Cu^{2+} sensor along-with those reported in the literature is summarized in Table 5. It is clear from Table 5 that the present studies have helped in developing better sensor than existing sensors for Cu^{2+} in terms of working concentration range [8, 11, 12], pH range [10, 11], response time [11], lifetime [12] and application to real sample analysis [7–12, 16].

Acknowledgement

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