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Chelating ionophore based membrane sensors for copper(II) ions

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Abstract

Acetylacetone, ethylacetoacetate and salicyldehyde, are reported to form chelates with copper of high stability as compared to other metals. Therefore, PVC based membranes of bis[acetylacetonato] Cu(II) (**A**), bis[ethylacetoacetate] Cu(II) (**B**) and bis[salicyldehyde] Cu(II) (**C**) have been investigated as copper(II) selective sensors. The addition of sodium tetraphenylborate and various plasticizers, viz., DOS, TEHP, DOP, DBP and TBP have been found to substantially improve the performance of the sensors. The membranes of various compositions of the three chelates were investigated and it was found that the best performance was obtained for the membrane of composition **A** (1%): PVC (33%): TBP (65%): NaTPB (1%). The sensor shows a linear potential response to Cu(II) over wide concentration range 2.0×10^{-6} to 1.0×10^{-1} M (detection limit ~0.1 ppm) with Nernstian compliance (29.3 mV decade^{-1} of activity) between pH 2.6 and 6.0 with a fast response time of ~9 s. The potentiometric selectivity coefficient values as determined by match potential method (MPM) indicate excellent selectivity for Cu^{2+} ions over interfering cations. The sensor exhibits adequate shelf life (~3 months) with good reproducibility (S.D. ±0.2 mV). The sensor has been used in the potentiometric titration of Cu^{2+} with EDTA. The utility of the sensor has been tested by determining copper in vegetable foliar and multivitamin capsule successfully.

Keywords: Copper; Sensors; Chelates; Copper-selective electrodes; Copper ions

1. Introduction

Copper is widely used for industrial, agricultural and domestic purposes and is therefore present in environment. It is considered an essential element but is toxic at higher concentration level. The uptake of copper by human beings above certain level is known to cause gastrointestinal cattarch, Wilson disease, hypoglycemia, and dyslexia. The determination of copper is thus important in view of its utility as well as toxicity. A number of instrumental methods, such as AAS, ICP, stripping voltametry, and flame photometry are employed for the determination of copper at low concentration level. These methods, generally, require sample pretreatment and infrastructure backup and are not very convenient for routine analysis of large number of environmental samples. Ion sensors are the analytical tools which are convenient, fast and require no sample pretreatment and also suitable for 'on-line' analysis. As such, number of Cu^{2+} selective sensors using solid membranes of Cu(II) insoluble salts [1–3], copper chelates [4–12], macrocyclic polyethers [13,14], non-cyclic neutral ionophores containing dithiocarbamate groups [15,16], and calix[4]arenes [17,18] have been reported. Besides solid membrane electrodes, some liquid membranes involving copper(II) complexes [19–21] have also been prepared. However, most of the reported electrodes have limitations in that they exhibit interference to K^+ [13], Ag^+ [7,20], Hg^{2+} [7–9], Pb^{2+} [5,9,10,15,16], and Fe^{3+} [8] ions, work over narrow concentration range [2,9,18,21] and show non-Nernstian response [2,5,9], limited pH range [20] and high response time [2]. Thus, these electrodes could not be put to widespread use for Cu^{2+} estimation. Therefore, efforts are still needed to develop a more selective and sensitive sensor. 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

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particular metal ion. The limited availability of such materials makes it difficult to develop selective sensors. Ligands, forming chelates of higher stability with particular metal can be employed as suitable material for ion sensors. A survey of the literature reveals that acetylacetone, ethylacetoacetate and salicyldehyde form chelates with Cu(II) of higher stability [22,23]. Further, metal exchange reaction studies with chelates of these ligands have shown that they exhibit selective and rapid exchange for Cu(II) [23,24]. Thus, it is reasonable to expect that the copper chelates of these ligands could act as selective sensor materials for Cu(II). Therefore, PVC membranes based on bis[acetylacetonato] Cu(II), bis[ethylacetoacetate] Cu(II) and bis[salicyldehyde] Cu(II) have been investigated as Cu^{2+} sensor and the results are reported herein.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. Acetylacetone, ethylacetoacetate, salicyldehyde, bis(2-ethylhexyl)sebacate (DOS) and high molecular weight poly(vinyl chloride) (PVC), Aldrich, USA; sodium tetraphenylborate (NaTPB) and tri-*n*-butylphosphate (TBP), BDH, UK; dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel, India; tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), nitric acid and sodium hydroxide were obtained from Ranbaxy, India. Solutions of metal (nitrates) were prepared in double distilled water and standardized by the reported methods where ever necessary. Working solutions of different concentrations were prepared by diluting 0.1 M stock solutions.

2.2. Synthesis of chelates

The chelating ionophores, viz., bis[acetylacetonato] Cu(II) (**A**), bis[ethylacetoacetate] Cu(II) (**B**) and bis[salicyldehyde] Cu(II) (**C**) were prepared by the reported method [25]. **A** was prepared by adding drop wise a solution of acetylacetone (5 ml, 0.05 mmol) in methanol (10 ml) to a stirring solution of Cu(II) chloride dihydrate (4 g, 0.025 mmol) in distilled water (25 ml) over a period of 20 min. Sodium acetate (6.8 g) in distilled water (15 ml) was added to the resulting mixture over a period of 5 min. The reactants were heated under reflux for 45 min. The reaction mixture was cooled to room temperature. Blue product obtained was filtered, washed with distilled water and recrystallised from methanol. The chelates **B** and **C** were prepared analogous to **A**. For the preparation of **B** 1:2 molar ratio of Cu(II) chloride dihydrate and ethylacetoacetate was used whereas the same ratio of Cu(II) chloride dihydrate and salicyldehyde was used for the preparation of **C**. The purity of the chelates was confirmed via thin layer chromatography, UV–vis spectrophotometry and elemental analysis.

- (**A**) TLC: $R_f = 0.35$ (1% MeOH in CH_2Cl_2); $\lambda_{max} = 310$ nm; analytically calculated for $C_{10}H_{14}O_4Cu$: C, 44.88% and H, 5.35%; found: C, 44.70% and H, 5.29%.
- (**B**) TLC: $R_f = 0.30$ (1% MeOH in CH_2Cl_2); $\lambda_{max} = 253$ nm; analytically calculated for $C_{12}H_{18}O_6Cu$: C, 44.78% and H, 5.59%; found: C, 44.62% and H, 5.43%.
- (**C**) TLC: $R_f = 0.46$ (1% MeOH in CH_2Cl_2); $\lambda_{max} = 251$ nm; analytically calculated for $C_{14}H_{10}O_4Cu$: C, 54.98% and H, 3.27%; found: C, 54.78% and H, 3.12%.

2.3. Preparation of membranes

The PVC based membranes were prepared by dissolving appropriate amounts of copper chelates, anion excluder NaTPB, solvent mediators (DOS, TEHP, DOP, DBP and TBP) and appropriate amounts of PVC in THF (5–10 ml). After complete dissolution of all the components and thorough mixing, homogeneous mixture was poured into polyacrylates rings placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at room temperature. To obtain membranes with reproducible characteristics, the viscosity of the solution and solvent evaporation were carefully controlled otherwise morphology and thickness of the membranes has shown a drastic variation which ultimately affected the sensor response. The transparent membranes of 0.4 mm thickness were removed carefully from the glass plate. A 5 mm diameter piece was cut out and glued to one end of a “Pyrex” glass tube. The membranes thus prepared were equilibrated for 2–3 days in 0.1 M Cu^{2+} solution. Membranes of different compositions were prepared and investigated. Those, which gave reproducible results and best performance characteristics, were selected for detailed studies. The optimum composition of membranes performing best is given in Tables 1–3.

2.4. Apparatus and potential measurements

The potential measurements were carried out at 25 ± 0.1 °C with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrodes

$$\text{SCE/internal solution }(0.1\text{ M, }Cu^{2+})\text{/membrane/test solutions/SCE}$$

A GBS, Avanta atomic absorption spectrophotometer with air acetylene flame was used at 217.0 nm to analyze real samples.

2.5. Sample preparation

The concentration of copper was determined in vegetable foliar and multivitamin capsule by directly dipping the sensor in the sample solution after appropriate dilutions. A 0.5 g of foliar was dissolved in 20 ml distilled water by adding few

Table 1
Composition of PVC membranes of **A** and performance characteristics of Cu^{2+} selective sensors based on them

Sensor no.	Percentage (w/w) of various components in membranes								Working concentration range (M)	Slope (mV $decade^{-1}$ of activity)	Response time (s)
	A	PVC	NaTPB	DOS	TEHP	DOP	DBP	TBP			
1	1	33	1						2.8×10^{-5} to 1.0×10^{-1}	26.4	45
2	1	33	1	65					1.8×10^{-5} to 1.0×10^{-1}	27.0	28
3	1	33	1		65				1.4×10^{-5} to 1.0×10^{-1}	27.0	22
4	1	33	1			65			7.9×10^{-6} to 1.0×10^{-1}	27.0	17
5	1	33	1				65		5.6×10^{-6} to 1.0×10^{-1}	29.0	13
6	1	33	1					65	2.0×10^{-6} to 1.0×10^{-1}	29.3	09

Table 2
Composition of PVC membranes of **B** and performance characteristics of Cu^{2+} selective sensors based on them

Sensor no.	Percentage (w/w) of various components in membranes								Working concentration range (M)	Slope (mV $decade^{-1}$ of activity)	Response time (s)
	B	PVC	NaTPB	DOS	TEHP	DOP	DBP	TBP			
7	1	33	1						4.0×10^{-5} to 1.0×10^{-1}	25.0	52
8	1	33	1	65					3.1×10^{-5} to 1.0×10^{-1}	27.5	30
9	1	33	1		65				1.3×10^{-5} to 1.0×10^{-1}	27.0	26
10	1	33	1			65			1.0×10^{-5} to 1.0×10^{-1}	25.0	20
11	1	33	1				65		7.3×10^{-6} to 1.0×10^{-1}	28.0	18
12	1	33	1					65	5.5×10^{-6} to 1.0×10^{-1}	28.2	15

Table 3
Composition of PVC membranes of **C** and performance characteristics of Cu^{2+} selective sensors based on them

Sensor no.	Percentage (w/w) of various components in membranes								Working concentration range (M)	Slope (mV $decade^{-1}$ of activity)	Response time (s)
	C	PVC	NaTPB	DOS	TEHP	DOP	DBP	TBP			
13	1	33	1						7.9×10^{-5} to 1.0×10^{-1}	25.0	60
14	1	33	1	65					5.0×10^{-5} to 1.0×10^{-1}	26.0	35
15	1	33	1		65				3.5×10^{-5} to 1.0×10^{-1}	27.0	30
16	1	33	1			65			2.0×10^{-5} to 1.0×10^{-1}	27.0	26
17	1	33	1				65		1.7×10^{-5} to 1.0×10^{-1}	28.0	20
18	1	33	1					65	1.0×10^{-5} to 1.0×10^{-1}	28.5	15

drops of concentrated nitric acid. It was then filtered and diluted to100 ml with distilled water. The multivitamin capsule sample was prepared by dissolving it in10 ml concentrated nitric acid. The mixture was heated to dryness and then 10 ml distilled water with few drops of concentrated nitric acid was added. The solution was filtered and diluted to 100 ml with distilled water.

3. Results and discussion

3.1. Working concentration range and slope

The potentials of the membranes of the three chelates, viz., **A**, **B** and **C** were investigated as a function of Cu^{2+} activity and the results obtained are shown in Figs. 1–3. Tetraphenylborate was added to all the prepared membranes to reduce the interference from sample anions (Donnan exclusion), optimize sensing selectivity and to reduce bulk membrane impedance [26]. It is seen from Fig. 1 that the sensor no. 1 having the membrane of copper chelate **A** without plasticizer exhibits linear response over a working concentration range of 2.8×10^{-5} to 1.0×10^{-1} M with a slope of 26.4 mV $decade^{-1}$ of activity. The slope of the membrane is sub-Nernstian and the working concentration range is narrow. The improvement in the performance was attempted by the addition of plasticizers to the membranes. The addition of plasticizers not only improves the workability of

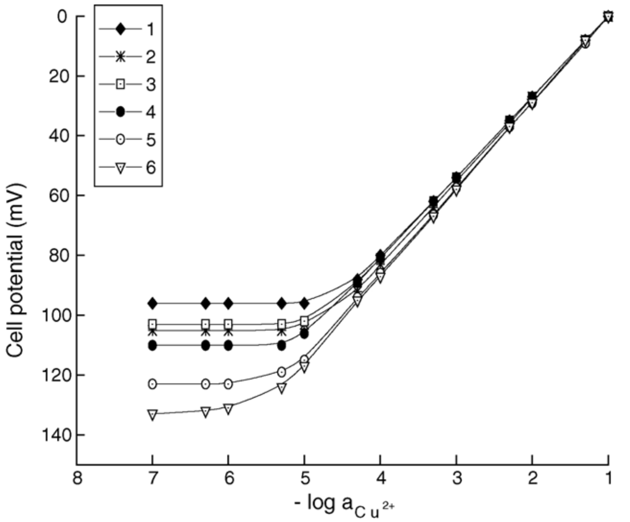

Fig. 1. Variation of membrane potential with activity of Cu^{2+} ions; PVC based membranes of **A** without solvent mediator (1), with solvent mediators, DOS (2), TEHP (3), DOP (4), DBP (5) and TBP (6).

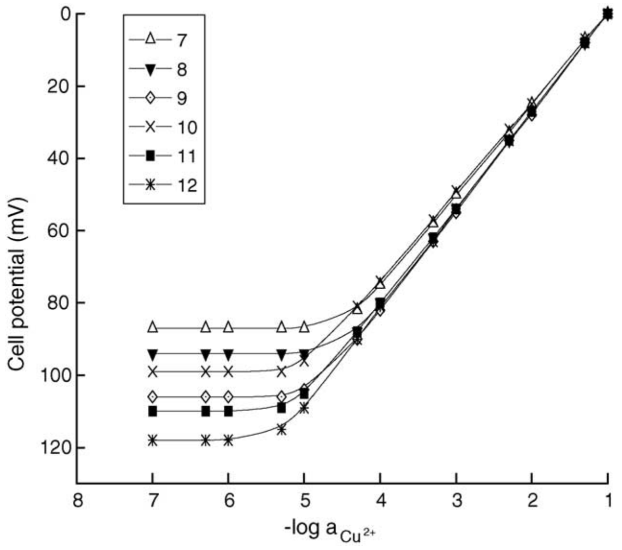

Fig. 2. Variation of membrane potential with activity of Cu^{2+} ions; PVC based membranes of **B** without solvent mediator (7), with solvent mediators, DOS (8), TEHP (9), DOP (10), DBP (11) and TBP (12).

the membranes but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [27,28]. However, the selectivity remains usually unaffected and mainly depends on the metal–ionophore interaction. The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate [29]. Thus, five plasticizers namely, DOS, TEHP, DOP, DBP and TBP were added in order to improve the performance of the sensors. The results obtained are shown in Fig. 1 and all performance characteristics of the sensors are compiled in Table 1. The addition of the five plasticizers to the membranes of **A** (sensor nos. 2–6) improved the working concentration range and the slope (Fig. 1 and Table 1). The best performance characteristics are obtained with the membrane having TBP plasticizer (sensor no. 6). This sensor exhibits the maximum working concentration range of 2.0×10^{-6} to 1.0×10^{-1} M with almost Nernstian slope of 29.3 mV decade^{-1} of activity. Similar studies carried out with the membranes of copper chelates **B** and **C**, with and without plasticizers, show that the addition of plasticizer improved the performance characteristics of the sensor. It is seen from Figs. 2 and 3 and Tables 2 and 3 that the sensors prepared with chelate B and C and containing plasticizer TBP perform best as they show widest working concentration range 5.5×10^{-6} to 1.0×10^{-1} and 1.0×10^{-5} to 1.0×10^{-1} M and almost Nernstian slope 28.2 and 28.5 mV decade^{-1} of activity, respectively. Repeated monitoring of potentials (15 measurements) at the same concentration (1.0×10^{-3} M) gave a standard deviation of ±0.2 mV. The performance of membranes without the ionophores was also investigated and it was seen that they generated no potential.

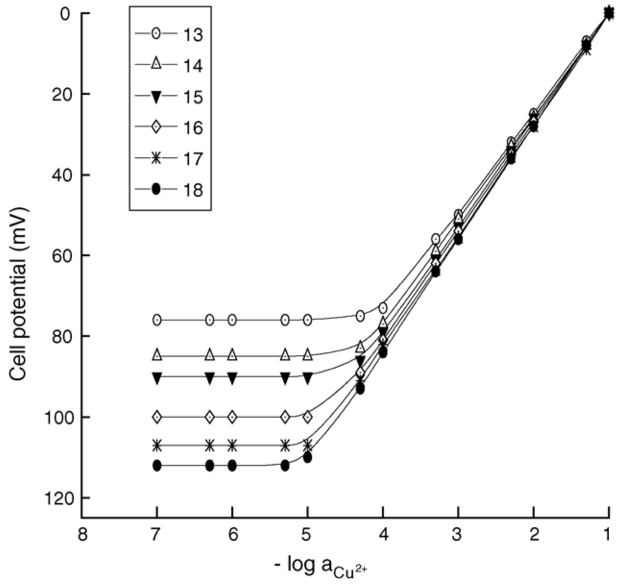

Fig. 3. Variation of membrane potential with activity of Cu^{2+} ions; PVC based membranes of **C** without solvent mediator (13), with solvent mediators, DOS (14), TEHP (15), DOP (16), DBP (17) and TBP (18).

3.2. Response and lifetime

The response time of the sensor has been determined by measuring the time required to achieve a steady potential for 10^{-4} M solution, when Cu(II) ion concentration was rapidly increased 10 fold from 10^{-5} to 10^{-4} M. Sensors having membranes (nos. 1, 7 and 13) without plasticizer gave a steady response in 45–60 s (Fig. 4). The addition of plasticizers to the membranes decreases the response time (Tables 1–3). Of all the plasticizers used, TBP improved the response time to the maximum extent. The response time of the membranes of chelates **A**, **B** and **C** with plasticizer TBP is found to be 9, 15 and 15 s, respectively. The main factor for the limited lifetime is the loss of one or more of its components, while contacting with aqueous solution. Sufficient lipophilicity of ionophore

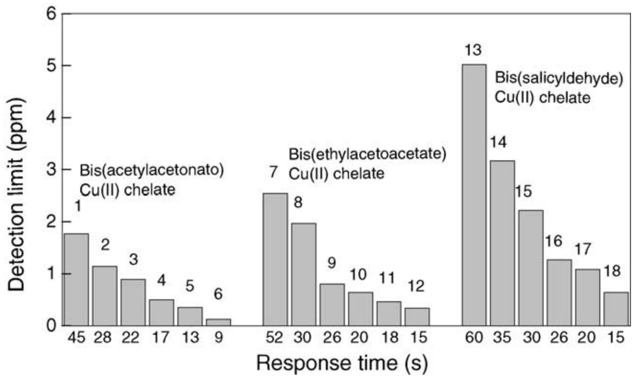

Fig. 4. Detection limit and response time of the membranes prepared from copper chelates of various compositions (sensor nos. 1–18).

Table 4
Selectivity coefficients of sensors 6, 12 and 18 based on the membranes of **A**, **B** and **C**, respectively

Interfering ion (j)	Selectivity coefficient (K_{ij}^{Pot})		
	Sensor no. 6	Sensor no. 12	Sensor no. 18
Na^+	1.5×10^{-2}	2.4×10^{-2}	6.2×10^{-2}
K^+	1.1×10^{-2}	2.9×10^{-2}	6.8×10^{-2}
Li^+	9.6×10^{-3}	1.2×10^{-2}	3.8×10^{-2}
Ag^+	1.2×10^{-2}	2.8×10^{-2}	8.4×10^{-2}
Ca^{2+}	7.4×10^{-3}	8.7×10^{-3}	4.6×10^{-2}
Mg^{2+}	9.1×10^{-3}	1.2×10^{-2}	2.7×10^{-2}
Ba^{2+}	5.5×10^{-3}	9.2×10^{-3}	3.2×10^{-2}
Ni^{2+}	4.8×10^{-2}	6.8×10^{-2}	9.1×10^{-2}
Hg^{2+}	8.7×10^{-3}	3.8×10^{-2}	4.2×10^{-2}
Cd^{2+}	1.2×10^{-2}	2.4×10^{-2}	7.5×10^{-2}
Mn^{2+}	1.8×10^{-2}	1.2×10^{-2}	6.8×10^{-2}
Co^{2+}	4.3×10^{-2}	6.3×10^{-2}	8.3×10^{-2}
Zn^{2+}	2.9×10^{-2}	3.2×10^{-2}	8.1×10^{-2}
Sr^{2+}	7.0×10^{-3}	9.4×10^{-3}	3.5×10^{-2}
Fe^{3+}	8.4×10^{-3}	1.0×10^{-2}	2.4×10^{-2}
Pb^{2+}	3.4×10^{-2}	6.5×10^{-2}	8.6×10^{-2}

and plasticizer ensures stable potentials and long lifetimes [27–29]. Among all the membranes prepared the lifetime of the membrane sensors comprising TBP was maximum and found to be 3 months for sensor of **A** (no. 6) and 2 months for sensors **B** and **C** (nos.12 and 18). During this lifetime of sensors no significant drift in potential was noticed. However, it is important to emphasize that the membranes were stored in 0.1 M Cu^{2+} solution when not in use.

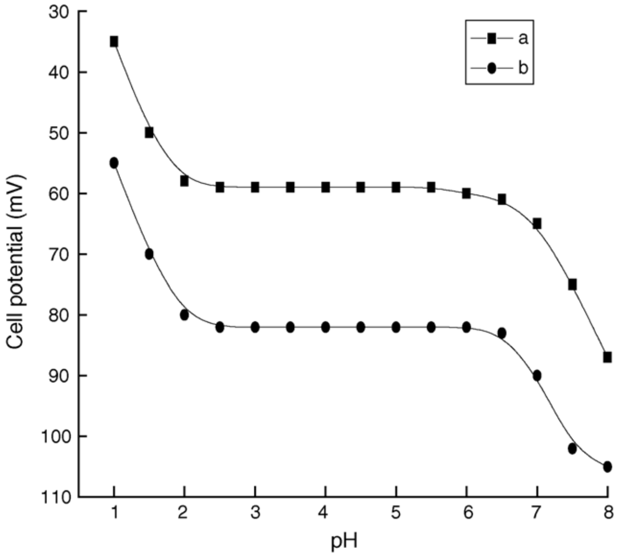

Fig. 5. Effect of pH on cell potential; $[Cu^{2+}] = 1.0 \times 10^{-3}$ M (a) and 1.0×10^{-4} M (b).

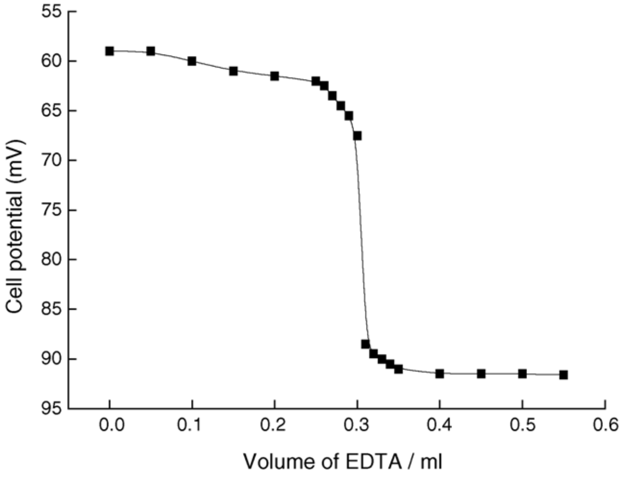

Fig. 6. Potentiometric titration plot of 1.0×10^{-3} M Cu^{2+} solution (30 ml) with EDTA (1.0×10^{-1} M).

3.3. *Potentiometric selectivity*

The selectivity studies for the membranes of chelates **A**, **B** and **C** were carried out only for sensors 6, 12 and 18 exhibiting the best performance characteristics in terms of working concentration range, slope, response time and lifetime. Match potential method (MPM) was used to determine potentiometric selectivity coefficients for these sensors. In the original procedure devised by Gadzekpo and Christian [30] the selectivity coefficient K_{ij}^{Pot} is given by the expression

$$K_{ij}^{\mathrm{Pot}} = a_i^{\mathrm{I}} - a_i/a_j$$

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^{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 a_i and a_i^{I} were kept at 2.0×10^{-5} and 8.0×10^{-5} M Cu^{2+} and a_j was experimentally determined. The values of selectivity coefficients so obtained are compiled in Table 4. It is seen from Table 4 that the three sensors investigated are highly selective to Cu^{2+} over a number of interfering ions. The log K values (K is the stability constant) of copper chelates **A**, **B** and **C** are reported to be 23.7, 14.2 and 13.0, respectively. The higher the stability constant the more selective the sensor is expected to be. Table 4 indicates that the selectivity values of the three sensors based on the membranes of chelates are in the order of **A** > **B** > **C** which in accordance to

Table 5
Quantification of copper in vegetable foliar and multivitamin capsule using AAS and Cu^{2+} sensor (no. 6)

Samples	Concentration of Cu(II) as determined by AAS ($g\,l^{-1}$)	Concentration of Cu(II) as determined by the proposed sensor ($g\,l^{-1}$)
Vegetable foliar	4.36 ± 0.02	4.33 ± 0.03
Multivitamin capsule	0.98 ± 0.01	0.95 ± 0.02

Table 6
Comparison of the proposed Cu^{2+} sensor (no. 6) with the reported electrodes

Sensor no.	Reference	Detection limit (ppm)	Slope (mV decade^{-1} of activity)	Selectivity	Response time (s)	Life time (month)
1	[2]	63.0	20	Poor	30	NM[a]
2	[4]	0.10	29.1	Good	10	NM
3	[6]	0.50	29.9	Very good	11	6
4	[9]	0.63	27.2	Poor	NM	NM
5	[10]	0.50	29.5	Good	15	NM
6	[13]	0.06	29	Good	10	NM
7	[18]	1.9	Nernstian	Poor	NM	NM
8	[19]	0.60	Nernstian	Good	15	6
9	[20]	0.30	28.3	Good	40	8 days
10	[21]	3.1	Nernstian	Good	NM	NM
11	Proposed sensor	0.10	29.3	Very good	9	3

[a] Not mentioned.

stability constant values. Most of the reported sensors showed serious interference to Hg^{2+}, Ag^{+} and Fe^{3+} ions. However, the sensors under consideration indicate sufficient selectivity for Cu^{2+} even over these interferents. As the sensor no. 6 showed maximum selectivity, further studies were done on this system only.

3.4. Effect of pH and non-aqueous solvents

The pH dependence of response of the sensor no. 6 has been tested over the range 1.0–8.0 at two Cu^{2+} concentrations of 1.0×10^{-3} and 1.0×10^{-4} M Cu^{2+} (Fig. 5). The pH values were adjusted by adding small volumes of dilute nitric acid or sodium hydroxide solutions. The results presented in Fig. 5 shows that the potential is independent of pH in the range 2.6–6.0. Thus, the same is taken as the working pH range of sensor assembly.

The utility of the sensor was also investigated in partially non-aqueous media using methanol–water, ethanol–water and acetone–water mixtures. The sensor worked satisfactorily up to 25% (v/v) in partially non-aqueous medium without any appreciable change in working concentration range or slope. Higher concentration of non-aqueous content could not be explored due to leaching of the copper chelates from the membrane matrix.

3.5. Analytical applications

The utility of the sensor no. 6 was further investigated to determine copper in vegetable foliar and multivitamin capsule. The results are found to be in close agreement with those obtained by AAS (Table 5). Thus the sensor can be employed for Cu^{2+} quantification in real samples. The sensor has also been used as an indicator electrode in the titrimetric determination of copper ions. The titration plot obtained (Fig. 6) at pH 4.0 is of standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Cu–EDTA complex.

4. Conclusions

The investigations on PVC based membranes of three copper chelates, viz., **A**, **B** and **C** have shown them to be sufficiently selective for Cu^{2+} ions. Of the three chelates, the sensor no. 6 based on chelate **A** having maximum stability constant is found to be most selective and exhibits widest working concentration range, minimum response time and maximum shelf life. This sensor is comparable in most respects to good reported electrodes (Table 6) but superior to them in terms of selectivity over Hg^{2+}, Ag^{+} and Fe^{3+} ions. The sensor could be put to analytical use both by direct potentiometry as well as potentiometric titration.

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