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Cu(II) selective PVC membrane electrode based on zinc complex of Acetophenonethiosemicarbazone (ZATSC) as an ionophore

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ABSTACT

A PVC membrane based Cu(II) selective electrode was constructed using zinc(II) complex of Actophenonethiosemicarbazone (ZATSC) as a neutral carrier. The sensor exhibits a Nerstian response for Cu(II) ion over a wide concentration range of 1.0×10^{-8}*-* 1.0×10^{-1} *M with the slope of 29.5 mV/per decade having detection limit* 6.7×10^{-9} *M. It was relatively fast response time (<10s for concentration* $\geq1.0\times10^{-4}$ *and <15s for concentration of* $\geq1.0\times10^{-6}$ *M) and can be used for 9 months without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity and high sensitivity for Cu(II) over other mono, di and trivalent cations and could be used in a pH range of 1.5-12.3. It was also used successfully as an indicator electrode in potentiometer titrations and in the analysis of concentration of copper in the water of river Yamuna at different sites of Delhi.*

Keywords: Cu(II) electrode, PVC, ionophore potentiometry.

INTRODUCTION

Analytical methods for determining the heavy metal ions have been extensively studied due to their importance in biological processes [1-3]. Polymeric membrane ion selective electrode (ISEs) provides one of the most powerful sensing methods because it is possible to select various sensory element according to the charge and size of the target ion in clinical and environmental assays [4-7].The quick determination of minute quantities of ionic species by simple method has great importance in analytical chemistry. Potentiometric detection based on ion-selective electrode (ISEs) is the simplest of all and offers unique advantages such as simple design and operation, reasonable selectivity, fast response applicability to colored and turbid solution. Schiff base with N and O donor atoms are well known to form strong complexes with transition metal ions. Some of the Schiff bases are reported to form strong complexes with a specific ion due to geometric factor [8, 9]. Schiff base [10-13] and non macrocyclic complexes [14-19] have attracted increasing attention in solvent extraction [20, 21], as ion exchanger [22, 23] and in catalytic studies [24, 25]. The ISEs dynamic response is generated by selective complexation of the target ion by ionophor dispersed in a polyvinyl chloride (PVC) matrix. Based on the recent advance of host-guest chemistry, polymemeric membrane ISEs for copper ion have been extensively developed by the use of crown ethers [26, 27]and related macrocyclic hosts as well as acyclic ligand [28, 29].Because of copper absorption, some genetic defects have been found. The major role of copper in metabolisms oxidation (both in ionic and enzyme form); thus its role in respiration, atherosclerosis (per oxidation), and anemia's is important, high uptake of copper results Wilson's diseases [30].A variety of potential ion carriers have been employed in the construction of Cu(II)ion selective electrodes. These copper ion carriers include small size thia-crown ethers and acyclic neutral ionophore with dithiocarbamate groups [31], calyx-4 arenas [32, 33], and schiff bases [34,35].However most of these copper selective sensors suffer from the interfering effects of cations such as Zn^{2+},Cd^{2+},Hg^{2+},$Pb^{2+}$and Ag^{+}.

In the present paper we report the use of **z**inc complex of Acetophenonethiosemicarbazone (ZATSC) as an ionophore in potentiometric polymer membrane sensor responsive to Cu^{2+}.

MATERIALS AND METHODS

Experimental

Chemicals: Reagent grade high molecular weight PVC, tetrahydrofuran (THF), acetophenone, thiosemicarbazide,were used as received. Tris(2-ethylehexyl)phosphate (TEP), dioctylphthalate (DOP), n-benzyl acetate (NBA), Tri n-butyl phosphate (TNBP), Nitrobenzene (NB), Dibutylphthalate (DBP) and sodium tetraphenyl borate (NaTPB), and nitrate of all metal salts used (Merck) were of highest purity available and used without any further purification. Throughout double distilled deionized water was used. The water samples of river yamuna of Delhi region was collected from Ramghat (S-1), Soorghat(S-2), Laxmi Nagar Bridge (S-3) and Okhla Bridge (S-4) at different sites.

Physical Measurement: The C, H and N were analyzed on a carlo-Erba 1106 elemental analysis.Electron impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrophotometer, ^{1}H NMR spectra were recorded on a Hitachi FT-NMR, Model R-600 spectrophotometer using $CDCl_3$ as solvent. Chemical shift are given in ppm relative to tetra methylsilane. IR spectra (KBr) were recorded on a Bruker FT-IR spectrophotometer Model No. TEN 50R-27 spectrophotometer. A Perkin-Elmer Model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace was used.

Syntheses of ionophore: The hot ethanolic solutions (20 mL) of acetophenone (1.12 mL 0.01m mol), thiosemicarbazide (0.91g , 0.01m mol) with few drops of acetic acid were mixed with costant stirring .The mixture was refluxed at 80±5 °C. On cooling a cream coloured compound is separated out, it was filtered, washed several times with cold EtOH and dried in vacuum over P_4O_{10}.

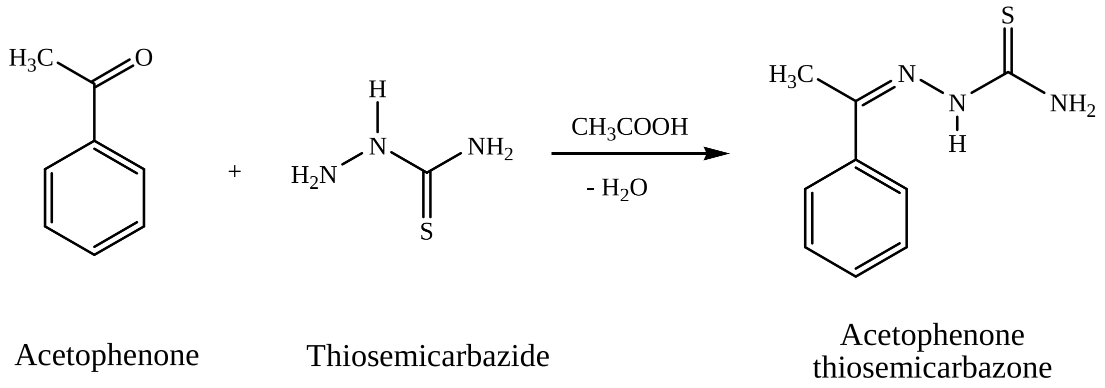


Fig.1: Syntheses of ionophore.

Acetophenonethiosemicarbazone: Yield (75.0%),M.P:181 °C, Anal. calc.for (%)= $C_9H_{11}N_3S$ C,55.06;H,5.76;N,21.76; S,16.59; Found: (%) : C;55.93;H,5.74;N,21.74; S,16.51; Mass.(m/z):193 (M^+) FT-IR (KBr): υ(NH_2) 3372 (b),υ(NH) 3178 (b), υ(C=N) 1510 , υ(C=S) 804 ; ^{1}HNMR ($CDCl_3$ 300 MHz): δ ppm=3.349(2H,s,- NH_2); 7.387-7.934(Ar-H); 2.502-2.292 (3H, CH_3).

Synthesis of complex (ZATSC): A hot aqueous ethanolic solution (20 mL 1:1 v/v) of acetophenone thiosemicarbazone (1.93 g, 0.02m mol) and a hot aqueous solution (20 mL) of zinc chloride (0 .068 g 0.01m mol) were mixed with constant stirring. The mixture was refluxed for about 6 hrs. On cooling a white colored precipitate was separated out. The same was filtered, washed with 50% ethanol and dried in vacuum over P_4O_{10}.

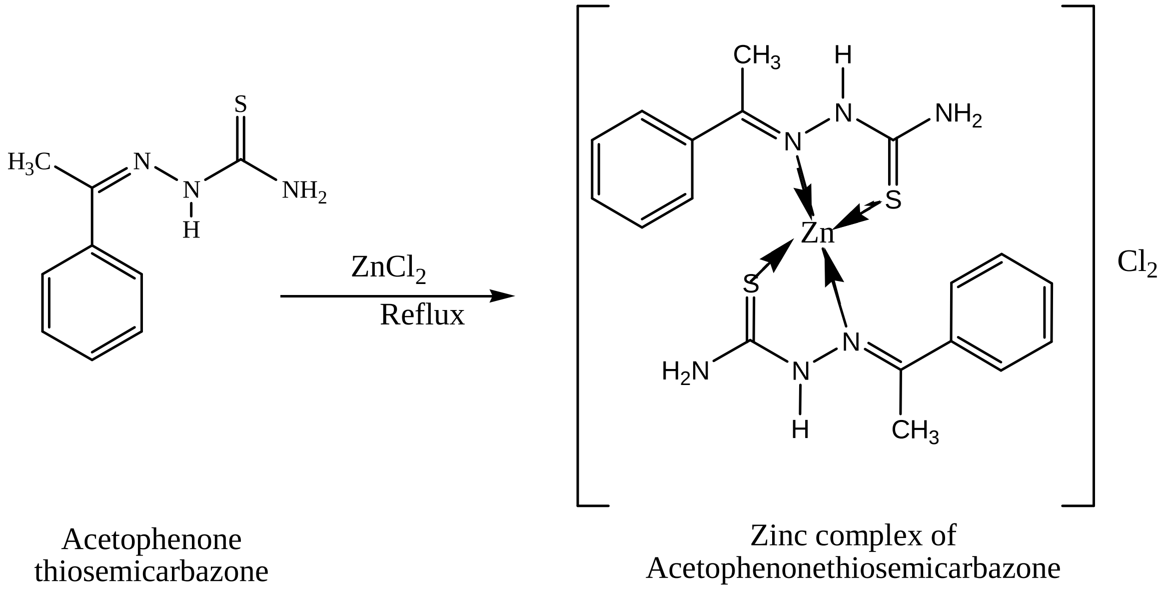


Fig.2: Synthesis of complex.

Zinc(II) Acetophenonethiosemicarbazone complex (ZATSC) : Yield (65%) M.P: 235 °C, Anal calc.for (%)= $C_{18}H_{22}N_6S_2ZnCl_2$: C,41.49; H,4.22; N,16.13; S,12.27 Found: (%) : C,41.41;H,4.21.N,16.1; S,12.21 Mass.(m/z):521.5(M^+) amu. FT-IR(KBr):υ(NH_2) 3297 (b),υ(NH) 3243 (b), υ(C=N) 1525 , υ(C=S) 834 ;

Potential Measurements:

All the membrane electrode potential measurements were performed at constant temperature (25 ±0.05 ^{0}C) using digital pH meter, potentiometer (ELICO L1-10, India) in conjugation with saturated calomel electrodes as reference electrodes. The representation of electrochemical cell for the EMF measurements is as follows.

External Reference Electrode (SCE)	Aqueous sample	Ion-selective membrane	Internal filling solution 1.0×10^{-2} M Cu(NO3)2	Internal reference solution (SCE)

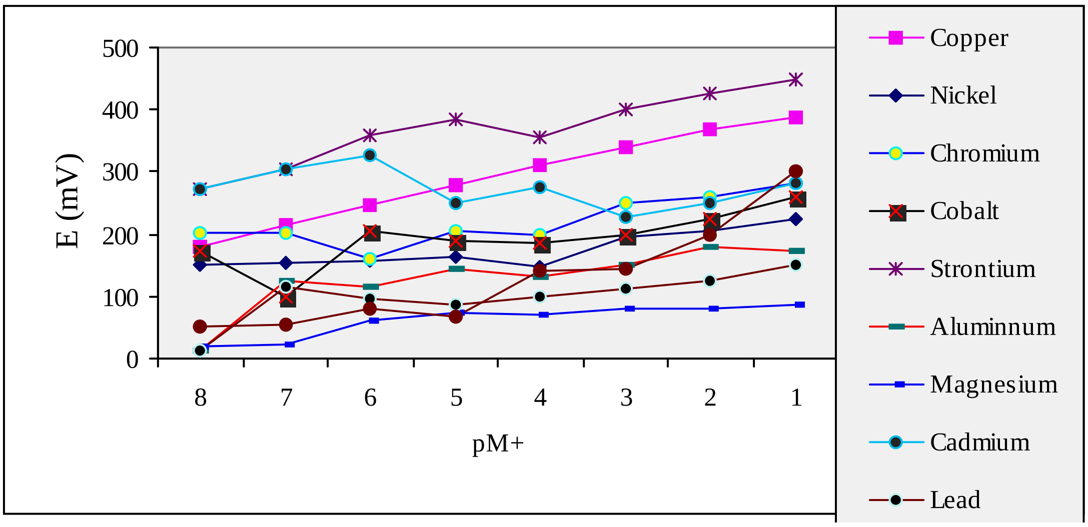
Electrode Preparation

The membranes were prepared by the method given by Craggs et.al. [36,37], with certain variations in composition of PVC, ionophore and plasticizers/solvent mediators like DBP, NB, DOP, TNBP etc. The PVC membrane solution was prepared by mixing of ionophore (5%wt.), TNBP as plasticizer (60%wt.), PVC (30%wt.) and NaTBP (5%wt.) dissolved in THF.The resulting mixture was poured into a Petridisc. The THF was allowed to evaporate at room temperature. A flexible membrane with a thickness of 0.2-0.4 mm was obtained. The discs of 6 mm diameter were cut and pasted to a Pyrex glass-tube with the help of Araldite. After getting dried, this tube was filled with 1.0×10^{-2} M internal solution of copper and immersed in the 1.0×10^{-2} M copper nitrate solution, at least for 2-3 days prior to use. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of the plasticizer used [38]. Thus, the ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized after a good deal of experimentation. Membranes, which generate reproducibility and stable potentials, have been studied. The blank membrane having only PVC as membrane ingredients was also prepared and studied. While membrane having PVC with plasticizer were generate small potential with slope of ~5mV/decade.

RESULTS AND DISCUSSION

Response of the cation:In preliminary experiment, response of the PVC based membranes of the ionophore to various cations was looked into and the potential generated are shown in Fig. 3. It has been observed that the membrane performs best with Cu^{2+} as the response is linear over a wide concentration (1.0×10^{-8} to 1.0×10^{-1} M). Thus, membranes used as Cu^{2+} sensor.

Fig. 3:



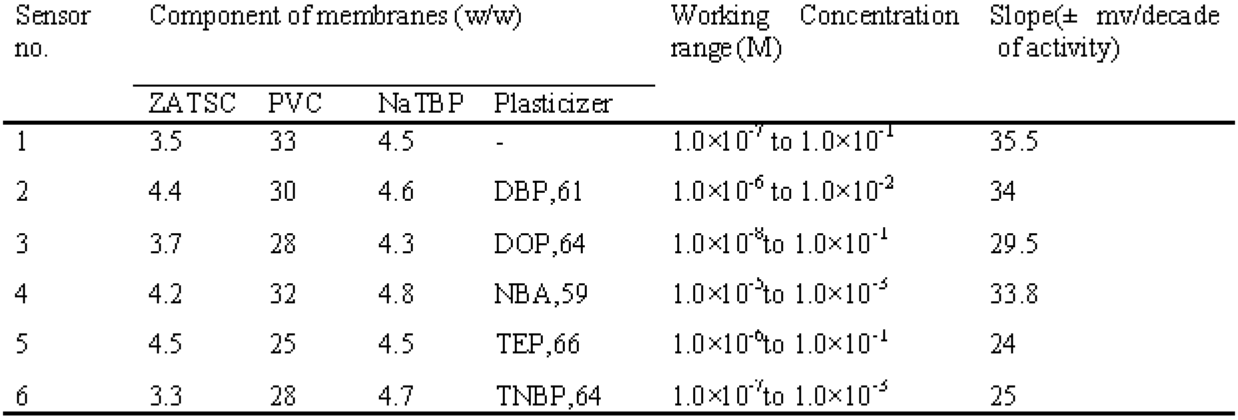
Potential response of various ion Selective electrodes based on ZATSC

Working concentration range and slope of Cu^{2+} sensor: Before starting any experimentation, the membranes were equilibrated with 1.0×10^{-2} M Cu^{2+} solution. The experiments have shown that 2 days equilibration time is required for generating reproducible and stable potential. The working concentration range and slope have been evaluated from these plots and summarized in Table 1. It has been observed (Fig. 3), that the membrane without plasticizer (sensor no. 1) having composition (3.5:33:4.5-ZATSC: PVC: NaTPB) (w/w%;) exhibits linear response to Cu^{2+}in the concentration range 1.0×10^{-7} to 1.0×10^{-1} M with a slope of 35.5 mV/decade of activity. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecular and state of compound [38], it was expected to play a key role in determining the ion-selective characteristics. So various plasticizer viz.DBP, TEP, DOP, NBA and TNBP were added in varying amounts to the membranes and ion-selective characteristics were studied. Also, the optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional membrane components [38, 39], therefore, NaTPB has also added to the membranes with the aim to improve the performance of the electrode. As shown in Table-1 that the addition of TEP and TNBP plasticizer (sensor no.5, 6) reduces the slope to 24.0 and 25.0 mV/decade of activity, whereas the performance of the membrane with DPB and NBA plasticizer (sensor no. 2, 4) is almost same as that of membrane without plasticizer (sensor no.1). The best performance is obtained with DOP plasticizer with membrane (sensor no. 3) having composition 3.7:28:4.3:64 (ZATSC: PVC: NaTPB: DOP) (w/w; mg). This sensor exhibits wide working concentration range of 1.0×10^{-8} to 1.0×10^{-1} M and detection limited 6.7×10^{-9} with a near-Nernstian slope of 29.5 mV/decade of activity.

pH and non-aqueous effect

The pH dependence of the electrode potential was tested over the range 0.5–14 for Cu^{2+}in this concentration 1.0×10^{-4} shown in Fig. 4. The pH of the solutions was adjusted by the addition of dilute hydrochloric acid or sodium hydroxide. It is clear from Fig. 4 that the useful pH range is 1.5–12.3, as the potentials remain constant in this range. The sharp change in potentials at higher pH values may be due to the hydrolysis of Cu^{2+}, while at lower pH values H^{+} ions start contributing to the charge transport process of the membrane, thereby, causing interference. The performance of the sensor no. 3 was also investigated in partially non-aqueous medium using methanol-water, ethanol-water, and acetone-water mixtures. The membrane worked satisfactorily in non-aqueous medium up to 20% (v/v) non-aqueous content as in these mixtures the working concentration range and slope remained unaffected as shown in Table-2. However, above 20% (v/v) non-aqueous content, slope, and working concentration range was reduced and potentials show drift. It is worth mentioning that the lifetime of the membranes did not alter in non-aqueous solutions.

Table-1 Composition of PVC membrane of (ZATSC) and performance characteristics of Cu^{2+}selective sensors based on them.



Sensor no.	Component of membranes (w/w)				Working Concentration range (M)	Slope(± mv/decade of activity)
	ZATSC	PVC	NaTBP	Plasticizer		
1	3.5	33	4.5	-	1.0×10^{-7} to 1.0×10^{-1}	35.5
2	4.4	30	4.6	DBP,61	1.0×10^{-6} to 1.0×10^{-2}	34
3	3.7	28	4.3	DOP,64	1.0×10^{-8}to 1.0×10^{-1}	29.5
4	4.2	32	4.8	NBA,59	1.0×10^{-5}to 1.0×10^{-3}	33.8
5	4.5	25	4.5	TEP,66	1.0×10^{-6}to 1.0×10^{-1}	24
6	3.3	28	4.7	TNBP,64	1.0×10^{-7}to 1.0×10^{-3}	25

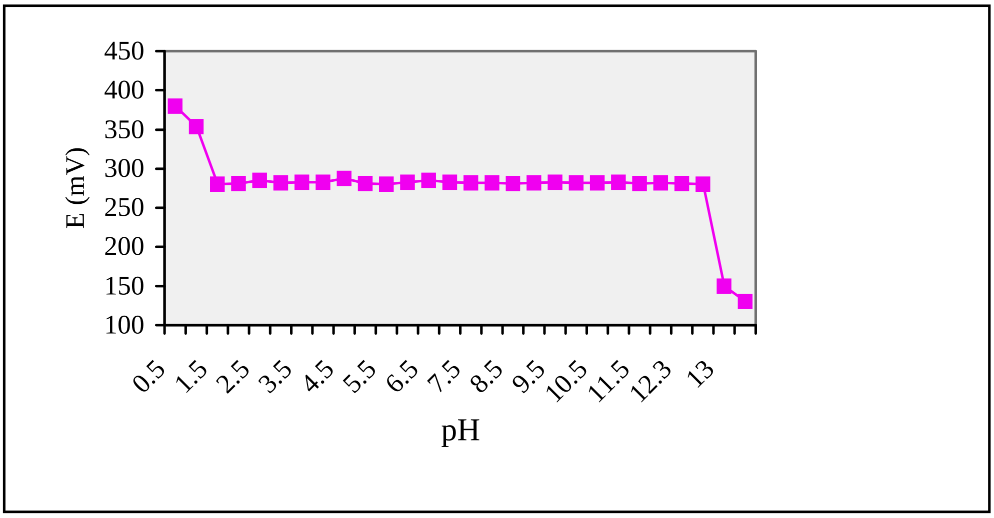


Fig.4: The effect of pH of test solution on the response of the Cu^{2+} ion selective electrode.

Table-2 Effect of partially non-aqueous medium on the working of Cu^{2+} selective sensors (sensor no. 3)

Non-aqueous content % (v/v)	Working concentration range (m)	Slope (±0.1mv/decade of activity)
Methanol		
10	1.0×10^{-8} to 1.0×10^{-1}	29.4
20	1.0×10^{-8} to 1.0×10^{-1}	29.5
30	1.0×10^{-8} to 1.0×10^{-1}	29.7
Ethanol		
10	1.0×10^{-8} to 1.0×10^{-1}	29.5
20	1.0×10^{-8} to 1.0×10^{-1}	28.4
30	1.0×10^{-8} to 1.0×10^{-1}	28.6
Acetone		
10	1.0×10^{-8} to 1.0×10^{-1}	29.4
20	1.0×10^{-8} to 1.0×10^{-1}	29.5
30	1.0×10^{-8} to 1.0×10^{-1}	29.6

Potentiometric selectivity

The selectivity is the most important characteristics, as it determines the extent of utility of a sensor in real sample measurement. The selectivity coefficient values were determined by fixed interference method (FIM), which was proposed by Saezde Viteri [40]. The selectivity coefficient values $K_{A,B}^{pot}$ indicate that the electrode is moderately selective to Cu^{2+} over a number of other cations (Table.3). The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, a_B, and varying activity of the primary ion, a_A. The potential values obtained are plotted vs. the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of a_A which is to be used to calculate $K^{pot}_{A,B}$ from the equation:

$$K^{pot}_{A,B} = (a_A/a_B)^{z_A/z_B}$$

Where both z_A and z_B have the same signs, positive or negative. a value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to primary as well as interfering ion. However, values smaller then 1.0 indicate that membrane sensor is responding more to primary ion than to interfering ions and in such a case the sensor is said to be selective to primary ion over interfering ion. Further, smaller is the selectivity coefficient, higher is the selectivity order. A perusal of Table 3 shows that selectivity coefficient values for the present sensor are much smaller than 1.0 over a number of mono, di and trivalent cations studied. Hence, the sensor is sufficiently selective over these ions and can therefore be used to estimate copper in presence of these ions by direct potentiometry.

Table-3: Selectivity coefficient values $K^{pot}_{A,B}$ for Cu^{2+} selective sensor by fixed interference method.

S. No.	Interfering ion (B)	Selectivity coefficients
1	K^+	1.01×10^{-3}
2	NH_4^+	4.03×10^{-3}
3	Cd^{2+}	2.44×10^{-3}
4	Pb^{2+}	8.03×10^{-4}
5	Hg^{2+}	4.03×10^{-4}
6	Ni^{2+}	1.11×10^{-4}
7	Zn^{2+}	5.12×10^{-3}
8	Co^{2+}	2.01×10^{-3}
9	Ca^{2+}	1.16×10^{-4}
10	Ba^{2+}	1.06×10^{-4}
11	Fe^{3+}	1.06×10^{-4}
12	Sr^{2+}	3.01×10^{-3}
13	Cr^{3+}	1.01×10^{-3}
14	Ag^{2+}	2.29×10^{-3}
15	Mg^{2+}	3.06×10^{-3}
16	Al^{3+}	6.01×10^{-4}

Response and lifetime. The average time required for the Cu^{2+} ion sensor to reach a potential with in ±1mV of final equilibrium value after successive immersion of a series of Cu^{2+}(II) ion solutions, each having a 10-fold difference in concentration, was measured. The static response time of the membrane sensor thus obtained was <10 s, for concentration $\geq 1.0\times10^{-4}$ and <15 s for concentration of $\geq 10^{-6}$(Fig-7). It should be noted that the equilibrium potential remain costent more than 8 min. The lifetime of the membrane sensor was about 9 months, during which it could be used without any measurable divergence.

The time of contact and concentration of the equilibrium 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 1.0×10^{-2} M and contact time of 2 days was appropriate for smooth functioning of the electrode. Membranes were stored in 1.0×10^{-2} M $Cu\ (NO_3)_2$ solution when not in used.

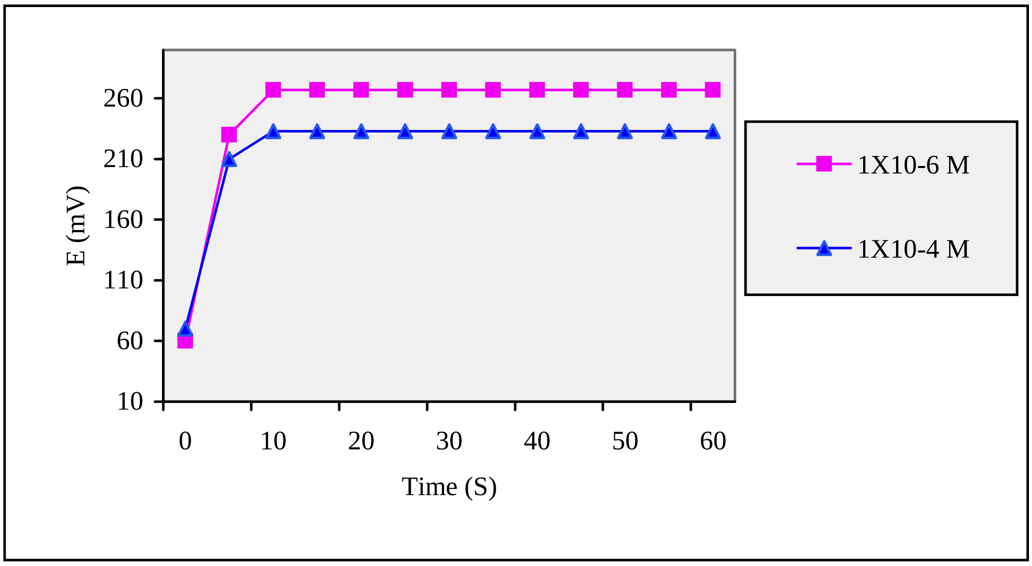


Fig.5: The effect of the time on potentiometric response of Cu^{2+} electrode.

Table-4 Comparison of the reported electrode with the reported electrode assembly

No	Woking concentration range/M	Slope	pH range	Res time/s	Life time/ month	Detection Limit	Ref.
1	1.0×10^{-1} to 8.0×10^{-6}	Not mention	3-6	< 60	>2	-	3
2	1.0×10^{-1} to 8.0×10^{-8}	29.3 ± 0.7	5-9	< 45	4	1.0×10^{-8}(mV/decade)	4
3	1.0×10^{-1} to 5.0×10^{-6}	29.6 ± 0.6	1.9-5.2	< 30	>4	0.3ppm	10
4	1.0×10^{-1} to 1.0×10^{-5}	30.0	3.3-7.0	< 35	3	0.5ppm	11
5	1.0×10^{-1} to 2.0×10^{-6}	29.3	2.6-6.0	9	3	0.1ppm	12
6	6.0×10^{-2} to 9.77×10^{-7}	30.0 ± 0.2	3.5-4.8	40	2	7.0×10^{-7}(mV/decade)	13
7	5.0×10^{-2} to 7.0×10^{-7}	30.0 ± 0.1	4-9	10	5	-	14
8	1.0×10^{-2} to 5.0×10^{-6}	28.3	3.6-7.8	-	3	-	15
9	5.0×10^{-3} to 1.0×10^{-6}	-	3.8-6.9	-	4	6.0×10^{-6}(mV/decade)	16
10	5.0×10^{-2} to 1.0×10^{-6}	29.5 ± 0.1	4.1-6.8	5	6	1.0×10^{-6}(mV/decade)	17
11	5.0×10^{-1} to 1.0×10^{-6}	29.5 ± 0.4	3.2-7.8	< 10	4-5	4.8×10^{-8}(mV/decade)	18
12	5.0×10^{-1} to 1.0×10^{-7}	29.5 ± 0.5	3-11	< 5	6-7	8.1×10^{-8}(mV/decade)	19
13	1.0×10^{-1} to 1.0×10^{-8}	29.5 ± 0.5	1.5-12.3	< 10	9	6.7×10^{-8}(mV/decade)	This work

3.7- Comparison with other reported electrodes

In Table 4, the response characteristics and the selectivity coefficients of the membrane electrode based on zinc complex of acetophenonethiosemicorbazone of some potential interfering ions are compared with the corresponding values previously reported [3] for copper ion-selective membrane electrodes based on a variety of different ionophores. As can be seen, the linear range and the response time of the proposed electrode are superior to those reported [4] for other copper ion-selective electrodes, and its selectivity behavior is among the most selective Cu^{2+} ion sensor reported [3,4,10-19]. At the same time, easy synthesis of a highly lipophilic macrocyclic and open chain ionophore in bulk, using easily and economically available starting materials, makes the proposed ISE a better membrane electrode.

Analytical applications

Potentiometric titration

The membrane sensor could be successfully used in the potentiometric titration of Cu^{2+} with EDTA. 20 mL (1.0×10^{-3} M) solution of Cu^{2+} was titrated with 1.0×10^{-5} M EDTA (Fig. 6). On the addition of EDTA, the concentration of Cu^{2+} ions decreases, causing a decrease in potential in line. However, the break point is sharp and corresponds to the stoichiometry of Cu (II)–EDTA complex. After the end-point, potentials are almost constant because now the sensor is not responding to small changes in Cu^{2+} concentration. Thus the electrode assembly can be used for copper ions determination by potentiometric titration.

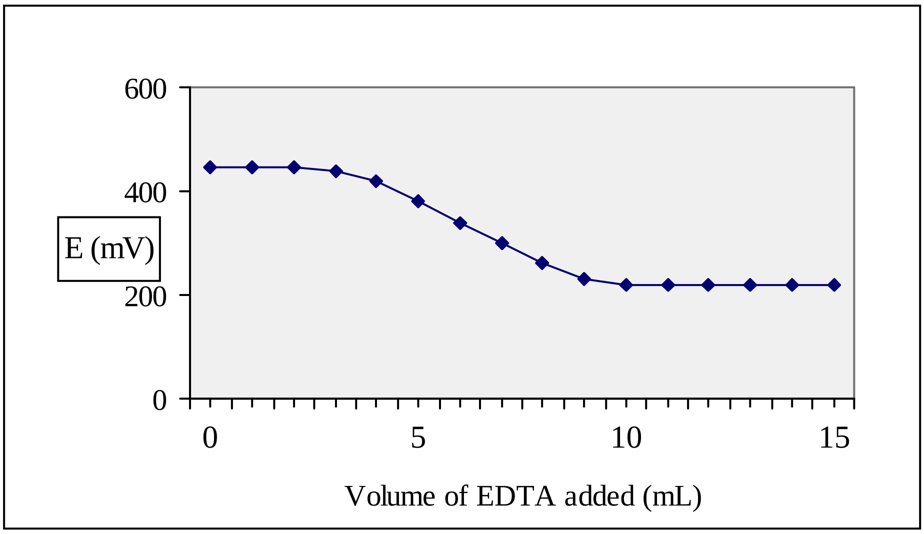


Fig.6. Potentiometric titration curve of Cu^{2+} ion (1.0×10^{-3} M, 20.0 mL) with EDTA (1.0×10^{-5} M), using the proposed sensor as an indicator electrode.

***Determination of Cu^{2+} in water sample*:**The proposed Cu^{2+} ion- selective electrode was found to work well under the laboratory conditions. It was successfully applied to the determination of copper from the water samples collected from the various sites of river Yamuna in Delhi region. The analysis of water samples does not required pretreatment for poteniometric determination using the present sensor. The pH of all samples is found between 5 to 8. The results observed for analysis were also compared with atomic absorption spectrometry (AAS) analysed sample. It is clear from the values in Table 5 that these were in a good agreement with the results obtained by AAS. Hence, the proposed sensor can be successfully employed for the estimation of copper ion.

Table-5 Determination of Cu^{2+} in water sample

Sample No	Copper found	
	ISE	AAS
S-1	0.0035 mg/l	0.0036 mg/l
S-2	0.0050 mg/l	0.0052 mg/l
S-3	0.0105 mg/l	0.0108 mg/l
S-4	0.0095 mg/l	0.0095 mg/l

CONCLUSION

The plasticized PVC-based membrane incorporating Zinc complex of acetophenonethiosemicarbazone as an ionophore, DOP as solvent mediator and NaTBP as anion excluder in a PVC matrix could be use to determine Cu^{2+} in the concentration range 1.0×10^{-8} to 1.0×10^{-1}M . The membrane was prepared using the fixed ratio of 3.7:28:4.3:64 (w/w) (ionophore:PVC:NaTBP:DOP). The detection limit was found to be 6.7×10^{-9} with a slope of 29.5 mV/decade of activity. The sensor works in a wide pH range 1.5 to 12.3 with a response time of 10 s. The selectivity of the electrode towards Cu^{2+} is quit well understood over the other cations. The lifetime of the assembly is 9 months in both aqueous and non aqueous medium. In addition to this, the membrane sensor can also be used as an indicator electrode in potentiometric titration involving copper(II) ions against EDTA as well as to determine Cu(II) quantitatively in the water samples of river Yamuna collected four different sites of Delhi.

Acknowledgements

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