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Copper(II) selective electrochemical sensor based on Schiff Base complexes

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Abstract

Plasticized membranes using Schiff Base complexes, derived from 2,3-diaminopyridine and *o*-vanilin have been prepared and explored as Cu^{2+}-selective sensors. Effect of various plasticizers viz., dibutyl phthalate (DBP), dioctylphthalate (DOP), chloronaphthalene (CN), tri-*n*-butylphosphate (TBP) etc. and anion excluder, sodium tetraphenylborate (NaTPB) was studied in detail and improved performance was observed at several instances. Optimum performance was observed with Schiff Base (B) having a membrane composition of B(1%):PVC(33%): DOP(65%):NaTPB(1%). The sensor works satisfactorily in the concentration range 5.0×10^{-6} to 1.0×10^{-1} M (detection limit 0.3 ppm) with a Nernstian slope of 29.6 mV per decade of activity. Wide pH range (1.9–5.2), fast response time (<30 s), high non-aqueous tolerance (up to 20%) and adequate shelf life (>4 months) indicate the vital utility of the proposed sensor. The potentiometric selectivity coefficient values as determined by match potential method (MPM) indicate good response for Cu^{2+} in presence of interfering ions. The tolerance level of Hg^{2+}, which causes serious interference in the determination of Cu^{2+} ions ($K^{\mathrm{Pot}}_{Cu^{2+}Hg^{2+}}$ (MPM): 0.45), was determined as a function of Cu^{2+} concentration in simulated mixtures. The sensor was also used in the potentiometric titration of Cu^{2+} with EDTA.

Keywords: Copper-sensors; Copper-selective electrodes; Schiff Base

1. Introduction

The utility of chemical sensors is being increasingly realized in view of rapid growth of industry vis-a-vis environment concern. In many frequently performed analyses, the use of sensors has made measurements feasible which are otherwise difficult to monitor and perform efficiently. Fast and accurate determination of copper is important in view of its widespread occurrence in diverse samples. A number of attempts have been made to develop Cu^{2+} selective sensor using solid membranes of copper(II) insoluble salts [1–3], copper chelates [4–6] and liquid membranes involving copper(II) complexes [7,8]. S-alkyl thioglycolic acid based electrodes were commercialised in 1960s [9,10], which soon after replaced by $CuS–Ag_2S$ based electrodes [11]. These electrodes suffered serious interference to Hg^{+}, Hg^{2+}, Ag^{+} and Fe^{3+} and to halides [12]. Kamata and coworkers [13,14] reported macrocyclic terathioether based electrodes, which resulted in a quite unsatisfactory selectivity for Cu^{2+} (log $K^{\mathrm{Pot}}_{\mathrm{Cu,K}}$(MSM): +1.1). Further, addition of pyridine group in macrocyclic dithioether also lead to poor selectivity. Some noncyclic ionophores with dithiocarbmate group [6,15] and neutral ionophores [16,17] containing nitrogen atoms have shown high affinity to Cu^{2+} ions in comparison to several transition metal ions, however, even these ionophores exhibit serious interference to Hg^{2+} ions. Hydroxamates compounds [18] and complexes of 6-nitroquinoxaline-2, 3 dithiol [19] with Cu^{2+} have been reported to exhibit lesser interference by Hg^{2+} and Ag^{+} ions. Recently, Gupta et al. have reported selective Cu^{2+} sensors exhibiting excellent selectivity for Cu^{2+} ions [20,21].

Sensors comprising Schiff Base as electroactive ingredient have been reported to exhibit excellent selectivity for Cu^{2+} ions. Schiff Bases upon deprotonation form complexes with Cu^{2+}, which act as charge carriers in the membrane matrix. These sensors have been reported to discriminate Hg^{2+} and Ag^{+} selectively [22]. In the present communication, Schiff Base prepared using 2,3-diaminopyridine and *o*-vanilin has been explored for the preparation of Cu^{2+} sensors and results are presented in the present paper.

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2. Experimental

2.1. Reagents

All reagents used were of analytical grade. High molecular weight poly(vinyl chloride) (PVC), Aldrich, USA; sodium tetraphenylborate (NaTPB), BDH, England; dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel India; dibuty(butyl) phosphonate (DBBP), Mobil, USA and 1-chloro-naphthalene (CN), E. Merck, Germany, were used without further purification. Metal (nitrates) solutions were standardized by use of appropriate methods and solutions of different concentrations were made by diluting 0.1 M stock solutions. Double distilled water was used throughout.

2.2. Apparatus

Potentiometric measurements were carried out at 25 ± 0.1 °C on a Mettler Toledo multichannel pH/ion analyzer (model MA235). The membranes were equilibrated for 2–3 days in 0.5 M Cu^{2+} solution and the potentials were measured using PVC matrix membranes in conjunction with saturated calomel electrodes (SCE) by setting up following electrochemical cell assembly:

Internal reference electrode (SCE)	Internal solution 0.1M Cu^{2+} pH~3.0	Membrane	Test solutions pH ~3.0- 4.0	External reference electrode (SCE)

Ionic strength of the solutions was maintained using 1.0 M KNO_3 as supporting electrolyte so as to minimize the concentration effect.

2.3. Preparation of Schiff Base

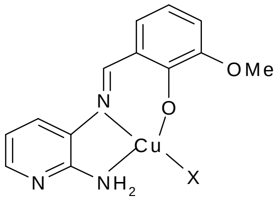
The Schiff Base compounds were prepared by the reported method [23].

2.3.1. DAPY-{Val H} (A)

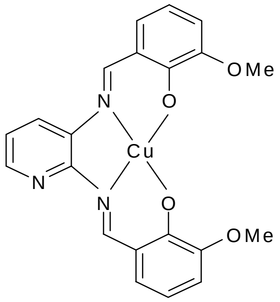
A was prepared by stirring equimolar solution of 2,3-diaminopyridine (0.501 g, 4.6 mM) and *o*-vanillin (0.699 g, 4.6 mM) in ethanol at room temperature for 2 h. Yellow product obtained was filtered, washed with ethanol and recrystallised from chloroform (yield 80%).

2.3.2. DAPY-{Val H}$_2$ (B)

B was prepared analogous to **A** by using 1:2 molar ratio of 2,3-diaminopyridine and o-vanillin (yield 75%).



A



B

These compounds were characterized by IR, ^1H NMR and elemental analysis.

2.4. Preparation of membranes

The membranes were prepared by dissolving Schiff Base **A** or **B** (1%), anion excluder NaTPB (1%), approximately 65% of solvent mediators (DBP, DOP, DBBP and CN) and appropriate amounts of PVC (33%) in THF (8–10 ml) (Tables 1 and 2). The optimum composition of the membranes was obtained after a good deal of experimentation. After complete dissolution of all the components and thorough mixing, the homogeneous mixture was poured into polyacrylates rings placed on a smooth glass plate. THF was allowed to evaporate at room temperature, after 24 h, transparent membranes of 0.5 mm thickness were obtained. A 5 mm diameter piece was cut out and glued to one end of a "Pyrex" glass tube. The membranes were further used for potential measurement studies.

3. Results and discussion

In preliminary investigations, Schiff base **B** was used as ionophore in PVC membrane for a number of metal ions including alkali, alkaline earth and transition metal ions. The potential response of various electrodes is shown in Fig. 1. Among these cations, the electrodes of alkali and alkaline earth metals show poor response whereas electrodes for transition metal ions exhibited near-Nernstian potential

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

Sensor no.	Percentage (w/w) of various components in membranes							Detection limit (ppm)	Slope (mV per decade)	Response time (s)
	(**A**)	PVC	NaTPB	DBP	DOP	DBBP	CN			
1	1	33	1	–	–	–	–	5.0	23.0	60
2	1	33	1	65	–	–	–	0.3	28.0	25
3	1	33	1	–	65	–	–	0.6	28.5	28
4	1	33	1	–	–	65	–	1.9	25.0	35
5	1	33	1	–	–	–	65	2.5	25.0	40

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

Sensor no.	Percentage (w/w) of various components in membranes							Detection limit (ppm)	Slope, (mV per decade)	Response time (s)
	(**B**)	PVC	NaTPB	DBP	DOP	DBBP	CN			
6	1	33	1	–	–	–	–	3.2	24.0	55
7	1	33	1	65	–	–	–	0.5	28.5	25
8	1	33	1	–	65	–	–	0.3	29.6	30
9	1	33	1	–	–	65	–	2.5	25.0	35
10	1	33	1	–	–	–	65	1.9	26.0	35

response. Among the transition metal ions the best response was observed for Cu^{2+} ions, therefore, the ionophore was selected as suitable sensor material for Cu^{2+}-selective sensor.

3.1. *Working concentration range and slope*

The performance characteristics viz., detection limit, slope, response time etc. for all the membrane electrodes (Nos. 1–10) are recorded in Tables 1 and 2. The membranes of different compositions of Schiff Base **A** and **B** exhibited linearity in the concentration range as shown in Figs. 2 and 3, respectively. In order to achieve perm-selectivity it is essential that no significant amount of counter ion should enter to the membrane phase. Lipophilic salt (sodium tetraphenylborate, NaTPB) was added to reduce the anionic interference and to lower the electrical resistance of the membrane. These lipophilic salts also exhibit ion-exchange properties and participate in the selective charge transport process if insufficient amount of ionophore is present.

Addition of appropriate amount of plasticizer leads to optimum physical properties and ensures high mobility of ions in the membrane. These solvent mediators strongly influence the working concentration range of the sensors. The lipophilicity, polarity, viscosity and dielectric constant of solvent mediator play a significant role in the optimization of the membrane ingredients so as to ensure the long and stable response by the sensor assembly [24–28]. The addition of solvent mediator DBP and DOP to the membrane of **A**, exhibited the enhanced working concentration range to 5.0×10^{-5} to 1.0×10^{-1} and 1.0×10^{-5} to 1.0×10^{-1} M with an improved slope of 28.0 and 28.5 mV per decade, respectively, (Fig. 2). Improvements in working concentration range and slope were also observed using Schiff Base **B** as membrane material, NaTPB as anion excluder and DBP and DOP as solvent mediators (Fig. 3). The effect of addition of various solvent mediators to the membranes of **A** and **B** is presented in Tables 1 and 2, respectively. Among all the membrane electrodes prepared, the best performance was obtained with the membrane having a composition of **B**(1%): PVC(33%): NaTPB(1%): DOP (65%) as it exhibited the wide working concentration range (5.0×10^{-6} to 1.0×10^{-1} M) with Nernstian compliance (29.6 mV per

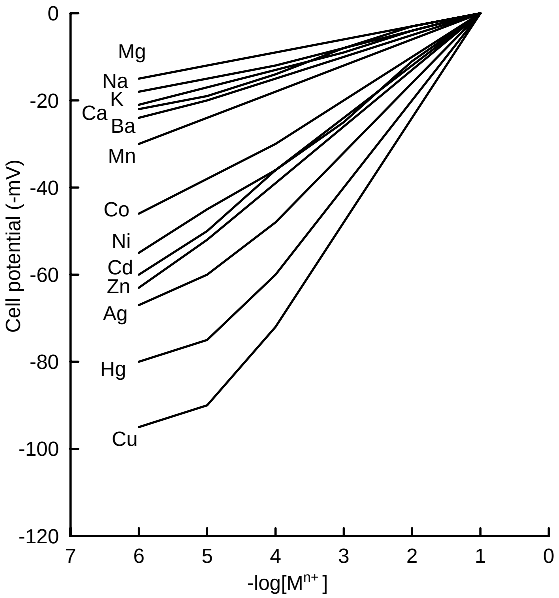


Fig. 1. Potential response of various ion-selective membranes based on Schiff Base (**B**).

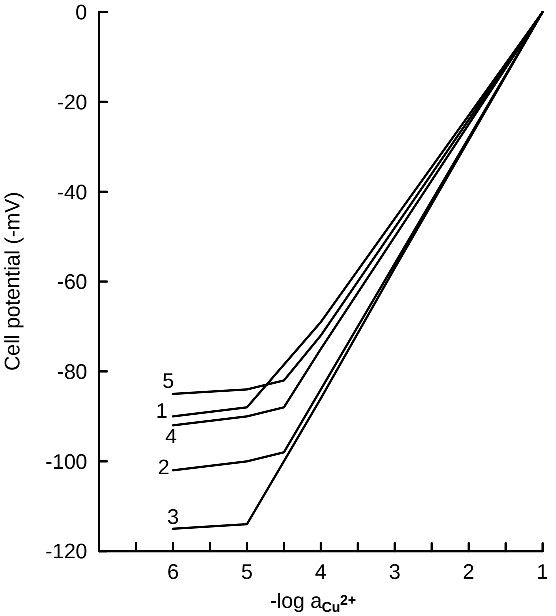


Fig. 2. Variation of cell potential with activity of Cu^{2+} PVC based membranes of Schiff Base (**A**) without solvent mediator (1), with solvent mediators, DBP (2), DOP (3), DBBP (4) and CN (5).

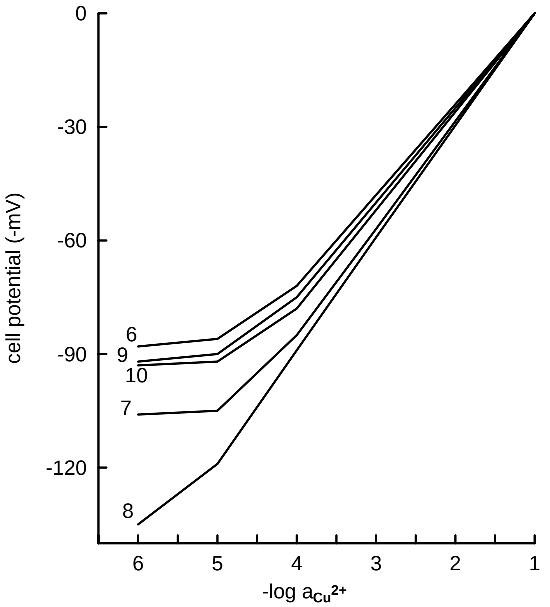


Fig. 3. Variation of cell potential with activity of Cu^{2+} PVC based membrane of Schiff Base (**B**) without solvent mediator (6), with solvent mediators, DBP (7), DOP (8), DBBP (9) and CN (10).

decade of activity). Therefore, the same membrane was selected for subsequent studies.

3.2. Response and lifetime

The response time is the time taken by the sensor to achieve a stable potential response and the same was measured by using flow-technique to create step activity change in the test solutions. Sensor without solvent mediator gave a steady response in 55–60 s while the sensors with plasticizers (DBP and DOP) as membrane ingredients achieved equilibrium response within 20–25 s over the whole concentration range. The main factor for limited lifetime of sensor is the loss of ionophores from the membrane matrix while contacting with aqueous solution. Optimum lipophilicity of the ionophore and plasticizer ensures stable potentials and long lifetime [24–26]. The membranes were used over a period of four months without significant change in potentials. Whenever a drift in potentials was observed, membranes were re-equilibrated with 0.5 M Cu^{2+} for 24 h. The membranes were stored in 0.1 M Cu^{2+} solution when not in use.

3.3. pH and non-aqueous effect

The dependence of sensor's potential response on the pH has been tested over the range 1.0 to 6.5 for 1.0×10^{-2} and 1.0×10^{-3} M Cu^{2+} solution (Fig. 4). The operational range was studied by varying the pH of the test solutions with nitric acid or ammonia. Fig. 4 shows that the potential is independent of pH in the range 1.9–5.2, therefore, the same was taken as the working pH range of the sensor assembly.

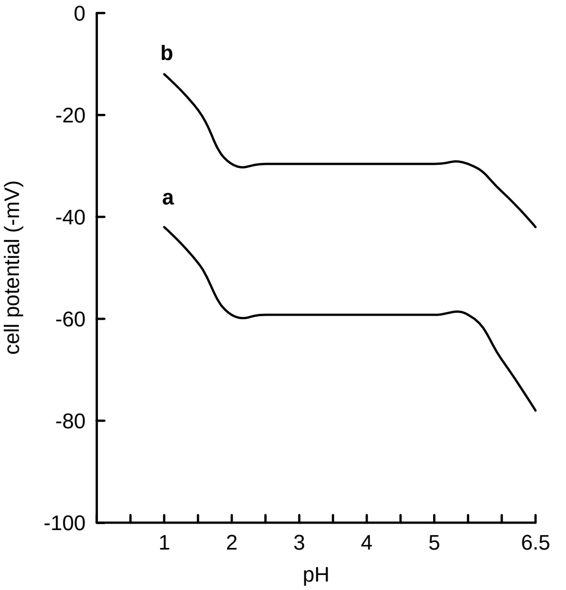


Fig. 4. Effect of pH on cell potential; $[Cu^{2+}] = 1.0 \times 10^{-3}$ M (a) and 1.0×10^{-2} M (b).

The performance of the sensor system was also investigated in partially non-aqueous medium using water–methanol mixture. The membrane worked satisfactorily up to a maximum 20% (v/v) content of methanol. In these mixtures, the working concentration range and slope remained unaltered, however, above a 20% non-aqueous content the slope decreased appreciably and reliable measurements could not be obtained. Also, the membranes were destroyed due to leaching of the ionophore from the PVC matrix.

3.4. Potentiometric selectivity

The selectivity is the most important characteristics, as it determines the extent of utility of any sensor in real sample measurement. As per Nicolskii–Eisenman formalism, the electrode response is given by the following simplified Nernst equation

$$E = E^0 + \frac{RT}{Z_1 F} \ln(a_i)$$

where a_i is the primary ion activity in pure solution, however, in presence of interfering ion Nernst equation is modified as follows

$$E = E^0 + \frac{RT}{Z_1 F} \ln(a_i + K_{i,j}^{\mathrm{Pot}} (a_j)^{Z_i/Z_j})$$

where a_j is the activity of interfering and Z_i and Z_j are the charges on the primary and interfering ion. As per IUPAC recommended match potential method (MPM) selectivity is given by

$$K_{ij}^{\mathrm{Pot}} = \frac{a'_{\mathrm{A}} - a_{\mathrm{A}}}{a_{\mathrm{B}}}$$

In this method, at first a known activity (a'_A) of the primary ion solution is added to a reference solution that contains fixed activity (a_A) of primary ion and the potential change is recorded. Secondly, a solution of interfering ions is added to the primary ion solution until the same potential change is observed. In the present studies a_A (1.0×10^{-3} M Cu^{2+}), a'_A (1.0×10^{-2} M Cu^{2+}) and a_B (1.0×10^{-2} M interfering ion) were taken to measure the selectivity coefficients. A perusal of selectivity values presented in Table 3 indicate that the sensor is selective for Cu^{2+} ions in presence of interfering ions except for Hg^{2+} and Ag^+ ions.

3.5. *Concentration dependence of Cu^{2+} versus Hg^{2+}*

To observe the concentration dependence of potentiometric selectivity coefficients, some mix solution studies were carried out so as optimize the concentration of interfering ions, which can be tolerated in the determination of Cu^{2+} ions [29–35] by the proposed sensor system. Hg^{2+}, Hg^+, Ag^+ etc. are reported to cause serious interference in the determination of Cu^{2+} ions. In order to determine the optimum tolerance level of Hg^{2+} ions, working concentration range for Cu^{2+} ions was determined in presence of different concentration of Hg^{2+} ions. The Cu^{2+} concentration was varied from 1.0×10^{-6} to 1.0×10^{-1} M while fixed concentrations of Hg^{2+} ions, i.e. 1.0×10^{-3}, 1.0×10^{-4} and 5.0×10^{-5} M were maintained in simulated mixtures. Fig. 5 indicates that the presence of Hg^{2+} above $<5.0 \times 10^{-5}$ M caused no deviation in the original working concentration plot, whereas at higher concentrations (1.0×10^{-4} and 1.0×10^{-3} M) divergence in the plots was observed. Therefore, Hg^{2+} at a concentration level $= 5.0 \times 10^{-5}$ can be tolerated over the whole concentration range, whereas at higher concentration, Cu^{2+} can be determined only over a reduced concentration range only. Similar studies were carried out for Ag^+ ions and the results presented in Fig. 6 show that the Ag^+ can be tolerated at a concentration level of $\leq 1.0 \times 10^{-4}$ M over the entire concentration range. Therefore, these studies indicate that the developed sensor is selective over the commonly present interfering ions unless they are present in higher quantities.

The interference of anions was also investigated, as halides are known to cause interference in the determination of Cu^{2+} ions. Fig. 7 shows that the presence of Br^- and Cl^-

Table 3
Selectivity coefficients values [$K^{Pot}_{Cu,B}$] obtained by Match Potential Method at 1.0×10^{-2} M interfering ion concentration level

Interfering ion (B)	Selectivity coefficients ($K^{Pot}_{Cu,B}$)
Li^+	4.5×10^{-3}
Na^+	8.5×10^{-2}
K^+	6.0×10^{-2}
Tl^+	7.8×10^{-2}
Cs^+	6.0×10^{-2}
Ca^{2+}	6.3×10^{-2}
Sr^{2+}	8.2×10^{-2}
Ba^{2+}	5.6×10^{-2}
Mg^{2+}	6.1×10^{-2}
Ag^+	5.4×10^{-1}
Hg^{2+}	4.5×10^{-1}
Ni^{2+}	7.5×10^{-2}
Cd^{2+}	8.2×10^{-2}
Zn^{2+}	8.1×10^{-2}
Co^{2+}	8.0×10^{-2}
Fe^{3+}	7.2×10^{-2}
Ce^{3+}	8.4×10^{-2}

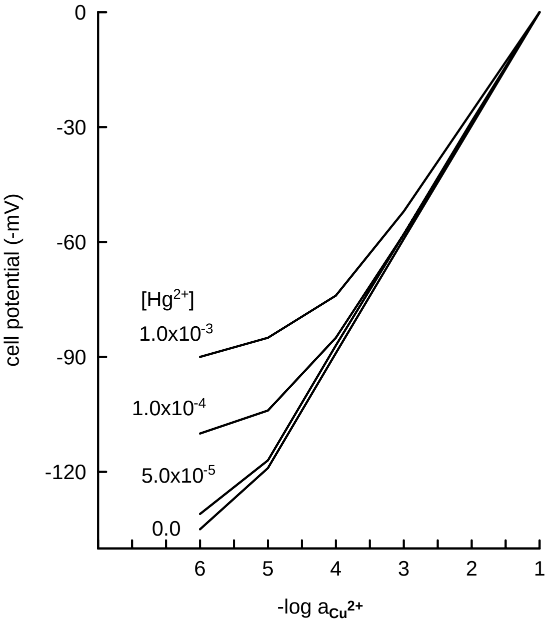


Fig. 5. Variation of cell potential with activity of Cu^{2+} at different concentration levels of Hg^{2+} ions.

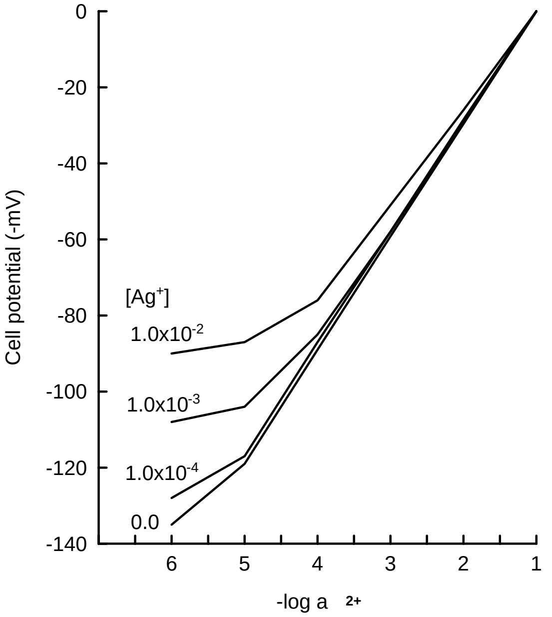


Fig. 6. Variation of cell potential with activity of Cu^{2+} at different concentration levels of Ag^+ ions.

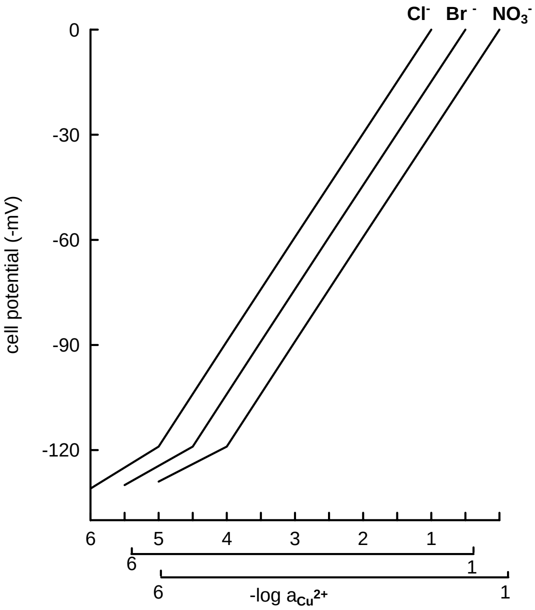


Fig. 7. Effect of anions; variation of cell potential with activity of Cu^{2+} ions.

ions does not cause any interference in the determination of Cu^{2+} ions. This may be attributed due to the addition of anion excluder, NaTPB, which prevents the interference of anions.

4. Potentiometric titration

The sensor was used to determine the end point in the potentiometric titration of Cu^{2+} with EDTA. The plots given in Fig. 8 are not of potentiometric type due to small interference of foreign ions. However, the sharp end-point corresponds to the stoichiometry of the Cu–EDTA complex and therefore, can be used for determining Cu^{2+} ions through potentiometry. The determination of Cu^{2+} could also be successfully carried out in presence of Hg^{2+} and Ag^{+} ions. Thus, these plots demonstrate the usefulness of the sensor for the potentiometric determination of Cu^{2+} ions in the presence of other metal ions.

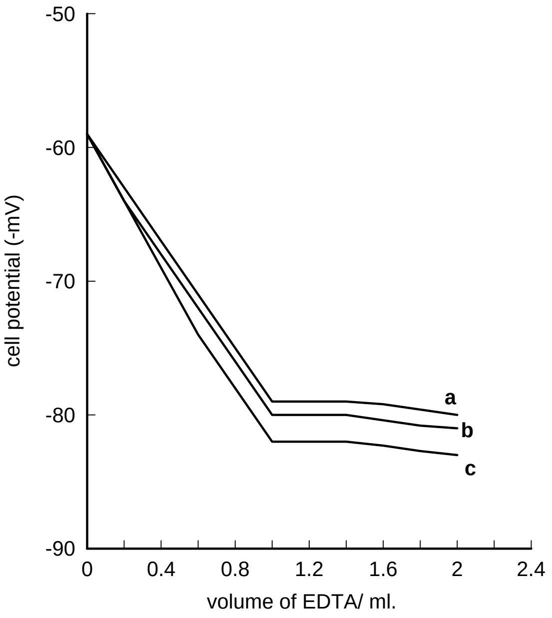


Fig. 8. Potentiometric titration plots of 1.0×10^{-3} M Cu^{2+} solution (10 ml): (a), 1.0×10^{-3} M Cu^{2+} + 1.0×10^{-4} M Hg^{2+} solution: (b), 1.0×10^{-3} M Cu^{2+} + 1.0×10^{-4} M Ag^{+} solution: (c) with EDTA (1.0×10^{-2} M).

5. Conclusion

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, response time, life time etc. and superior in the selectivity as it exhibits considerably less interference for commonly present cations viz., Hg^{2+}, Hg^{+}, Ag^{+} etc. and no interference to Br^{-} and Cl^{-} ions. Further, these sensors were used for the determination of Cu^{2+} in the presence of foreign ions both by direct potentiometry and titration.

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Table 4
Comparison of the proposed Cu^{2+} sensor with the reported electrodes

S. no.	Ref. no.	Detection limit (ppm)	Slope (mV per decade)	Response time (s)	Life time (month)	Selectivity
1	Jain et al. [3]	63.0	20	30	NM	Poor
2	Sun et al. [7]	0.60	Nernstian	NM	NM	Good
3	Kamata et al [14]	0.06	29	10	NM	Good
4	Brzozka et al. [16]	0.60	29	NM	NM	Good
5	Jain et al. [17]	0.60	28.5	30	5	Good
6	Pleniceanu et al. [19]	3.1	Nernstian	NM	NM	Good
7	Gupta et al. [20]	0.50	29.9	11	6	Very good
8	Ren [22]	0.30	28.3	40	8 days	Good
9	Proposed sensor	0.30	29.6	<30	>4	Very good

NM: not mentioned.

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References

[1] U.S. Lal, M.C. Chattopadhyaya, A.K. Dey, Ind. J. Chem. 19A (1980) 390.
[2] S.K. Srivastva, N. Pal, R.P. Singh, S. Agarwal, Ind. J. Chem. 23A (1983) 1033.
[3] A.K. Jain, P. Singh, L.P. Singh, Ind. J. Chem. 33A (1994) 272.
[4] K. Nagashima, I. Guo, T. Hobo, Bunseki Kagaku 41 (1992) 153.
[5] G.A. Askerov, F.M. Chyragov, D.G. Gamborov, A.M. Ayubova, Zh. Anal. Khim. 47 (1992) 337.
[6] S. Kamata, H. Murata, Y. Kubo, A. Bhale, Analyst 114 (1989) 1029.
[7] C.Q. Sun, Y.P. Sun, X. Zhang, H.D. Xu, J.C. Shen, Anal. Chim. Acta 312 (1995) 207.
[8] A.V. Gordievskii, A.Ya. Syrchenkov, N.I. Savvin, V.S. Shterman, S.V. Chizhevskii, A.F. Zhukov, Trudy Mosk Khim. Tekhnol. Inst. 69 (1972) 140.
[9] J.W. Ross, US Patent 3,497,424, Chem. Abstr. 72 (1970) 117229j.
[10] G.A. Rechnitz, Z.F. Lin, Anal. Lett. 1 (1967) 23.
[11] P. Buhlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1626.
[12] D.A. Roman, L. Rivera, Marine Chem. 38 (1992) 165.
[13] S. Kamata, M. Higo, T. Kamibeppu, I. Tanaka, Chem. Lett. (1982) 287.
[14] S. Kamata, K. Yamasaki, M. Higo, A. Bhale, Y. Fukunaga, Analyst 113 (1988) 45.
[15] S. Kamata, F. Ogawa, M. Fukumoto, Chem. Lett. (1987) 533.
[16] Z. Brzozka, Analyst 113 (1988) 891.
[17] A.K. Jain, V.K. Gupta, B.B. Sahoo, L.P. Singh, Anal. Proc. 32 (1995) 99.
[18] N.M. Sheina, N.V. Shvedene, L.B. Kulakova, J. Anal. Chem. USSR 45 (1990) 80.
[19] M. Pleniceanu, M. Preda, N. Muresan, L. Simoiu, Anal. Lett. 29 (1996) 1485.
[20] V.K. Gupta, R. Prasad, A. Kumar, Talanta 60 (2003) 149.
[21] V.K. Gupta, R. Prasad, A. Kumar, J. Appl. Electrochem. 33 (2003) 381.
[22] K. Ren, Talanta 36 (1989) 767.
[23] L.K.W. Henri, J. Tagenine, B.M. Gupta, Ind. J. Chem. 40A (2001) 999.
[24] W. Zhang, L. Jenny, U.E. Spichiger, Anal. Sci. 16 (2000) 11.
[25] P.C. Meier, D. Ammann, W.E. Morf, W. Simon, in: J. Koryta (Ed.), Medical & Biological Application of Electrochemical Devices, Wiley, 1980, p. 19.
[26] O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf, W. Simon, Anal. Chem. 63 (1991) 596.
[27] S. Jadav, E. Bakker, Anal. Chem. 73 (2001) 80.
[28] M.A.A. Perez, L.P. Martin, J.C. Quintana, M. Yazdani-Pedram, Sens. Actuators B 89 (2003) 262.
[29] S.K. Srivastava, V.K. Gupta, S. Jain, Anal. Chem. 68 (1996) 1272.
[30] S.K. Srivastava, V.K. Gupta, S. Jain, Analyst 120 (1995) 495.
[31] A.K. Jain, V.K. Gupta, B.B. Sahoo, L.P. Singh, U. Khurana, Analyst 122 (1997) 583.
[32] V.K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, Anal. Chim. Acta 355 (1997) 33.
[33] K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, P. Kumar, Anal. Chim. Acta 379 (1999) 201.
[34] L.P. Singh, J.M. Bhatnagar, Sensors 3 (2003) 393.
[35] L.P. Singh, J.M. Bhatnagar, J. Appl. Electrochem. 34 (2004) 391.