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Design and construction of ion-selective electrode based on a new Schiff base and its application in determination of copper(II) ions

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A copper(II) selective sensor has been made from polyvinyl chloride matrix membrane based on the carrier, 2-(5-bromo-2-hyroxybenzylidineamino) pyridine 3-ol as an ionophore, *ortho*-nitrophenyl octyl ether (o-NPOE) as mediator solvent and sodium tetraphenylborate (NaTPB) as additive. The best performance is presented by membrane of composition of ionophore (Schiff base):PVC:*o*-NPOE:NaTPB of 3:33:63:1 (by weight). The membrane potential response is linear in the concentration range of 1.0×10^{-7} to 1.0×10^{-2} *M* with the Nernstian slope of 29.5±0.5 mV per decade of Cu^{2+} and a detection limit of 7.4×10^{-8} *M*. The response time of the sensor is very short; less than 10 s, and it can be used for at least 8 weeks without any difference in potential. The proposed copper(II) selective electrode displays excellent selectivity towards alkali, alkaline earth and transition metal ions and can be used in the *p*H range of 4-7. It has been successfully used as an indicator electrode for the determination of Cu(II) in water samples. The electrode has also been employed as an indicator electrode in titration of Cu^{2+} with EDTA.

Keywords: Electrochemistry, Electroanalytical chemistry, Ion-selective electrodes, Schiff bases, Potentiometry, PVC-membrane, Copper

Copper is an essential micronutrient for living organisms and plays an important role in various ecosystems. The copper chemistry in aquatic systems is an intricate pattern that includes precipitation, complexation and redox reactions. It is well known that free copper ion (Cu(II)) is highly toxic to marine organisms and its determination in environmental samples is important[1-4]. A number of methods, such as atomic absorption spectrometry (AAS), cold vapor AAS or flame atomic absorption spectrometry-electrothermal atomization (AAS-ETA)[1-4], inductively coupled plasma optical emission spectrometry (ICP-OES)[5], anodic stripping voltammetry[6], chromatography[7], gravimetric detection[4] or photometry[4,8-12] are being used to determine its lowest level of concentration. However, while these approaches would provide accurate results, these are not very suitable for the analysis of a large number of environmental samples as generally sample pre-treatment and sufficient infrastructure backup is need. Ion-selective electrodes (ISEs) provide an alternate analytical method to such situations as they are fast, convenient, require minimal sample pre-treatment and may also be appropriate for online analysis.

Ion-selective electrodes (ISEs) are potentiometric sensors characterized by the electrochemical response which is usually dominated by one type of ion presented in solution known as primary ions (analyte ions, target ions), although other interfering ions, may also contribute to the membrane potential[1]. Copper-selective electrodes are the most important and most useful ISEs[1,3,15]. Although there are some reports in the field of copper-selective electrode[1-4], there are only a few reports on its application in clinical, pharmaceutical and environmental samples. Several types of ion carriers such as small size thiacrown esters[16], non-cyclic dithiocarbamate groups containing neutral ionophores[17,18], calix[8], arenes[19,20] and the Schiff base[21] have been employed in copper(II)-selective electrodes. Schiff base compounds have recently attracted attention in the ion selective sensors because of the presence of different donor atoms, the size of the cavity, the ligand to guest geometry, significant selectivity, sensitivity and stability for particular ions. Schiff base has been used as an ionophore in PVC-based sensors for the determination of transition metal ions such as Hg^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+}. In the present study, the Schiff base 2-(5-bromo-2-hyroxybenzylidineamino)pyridine 3-ol is used as a carrier for the construction of new graphite electrode for copper(II) ion. The effect of the membrane composition on the potential response of the Cu^{2+} sensor has been studied.

Experimental

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), *ortho*-nitrophenyl octylether (*o*-NPOE), sodium tetraphenylborate (NaTPB), oleic acid (OA), tetrahydrofuran (THF) and high relative molecular weight polyvinyl chloride (PVC) were purchased from Merck Chemical Co (Darmstadt, Germany). Metal nitrate salts (all from Merck) with the highest purity available were used without further purification. Nitric acid (0.1 *M*) and sodium hydroxide (0.1 *M*) were used to control *p*H. All experiments were carried out with doubly distilled deionized water.

The Schiff base, 2-(5-bromo-2-hyroxybenzylidineamino) pyridine-3-ol, was prepared as reported as reported in the literature.[22]

Typically, 25 mmol (0.050 g) of 5-bromo-2-hydroxy benzaldehyde dissolved in 5 mL methanol was added slowly to 0.25 mmol (0.027 g) of 2-amino-3-hydroxy pyridine in 3 mL methanol. After stirring, the resulting orange solution was heated and stirred for 10 min at 60 °C. The orange precipitate obtained after a day was washed with methanol and dried at room temperature. The reaction yield was 87% (0.066 g). FT-IR spectra for the synthesized Schiff base include peaks at 3448 (vs), 1628 (s), 1577 (m), 1544 (m) and 1521 (m) cm^{-1}.

The membrane solution was prepared by dissolving 33.0 mg of PVC powder, 63.0 mg of plasticizer o-NPOE, 1.0 mg NaTPB and 3.0 mg Schiff base of 2-(5-bromo-2-hyroxybenzylidineamino) pyridine 3-ol base in 5 mL of THF. The mixture was transferred into a glass jar and the solvent was evaporated slowly until a thick oil was obtained. Graphite electrodes were soaked in the oil blend for about 10 s, when non-transparent film of thickness 0.3 mm was formed. The graphite electrodes were then extracted from the mixture and kept at room temperature. After 2-3 h, the graphite electrodes was conditioned for 24 h by soaking in 1.0×10^{-4} *M* solution of $Cu(NO3)_2$.

The electrochemical system for the use of proposed electrode can be represented as follows: Ag|AgCl (sat.), KCl (3 *M*)|internal solution ($Cu(NO_3)_2$ (1.0×10^{-4} M))|PVC membrane test solution| Hg_2Cl_2 (sat.)|Hg.

A multimeter (Hioki 3803, Japan) was used to measure the potentials at 25.0 °C. All measurements were carried out in a 50 mL glass cell with constant magnetic stirring of the test solution. Activity was calculated according to the Debye-Huckel equation[23].

$$\log\gamma = \frac{-0.51z^2\sqrt{\mu}}{1+\sqrt{\mu}},$$ where γ is the ion activity coefficient, μ and z are ionic strength and charge of the ions, respectively.

Results and discussion

The response of the membrane electrode based on 2-(5-bromo-2-hyroxybenzylidineamino) pyridine-3-ol as a carrier in plasticized PVC membrane was found to be higher toward copper(II) ion as compared to other metal ions (Supplementary Data, Fig. S1). The efficiency of electrode for copper(II) ion was hence studied in detail. To test the performance characteristics of the membrane, the effect of membrane composition and the operational parameters such as selectivity, response time, sensitivity, life time, dynamic range and solution *p*H were studied.

It is well known that the sensitivity, linearity and selectivity of the PVC-membrane electrode depend to a large extent on the membrane composition and nature of the plasticizer and additive[24]. The effects of the amount of ionophore, the nature and amount of plasticizer and lipophilic additive on the potential response of Cu^{2+} sensors are summarized in Table 1. Amongst the different compositions studied, the membrane containing 33% PVC, 63% *o*-NPOE, 1% NaTPB and 3% Schiff base 2- (5-bromo-2-hyroxybenzylidineamino) pyridine 3-ol showed better response with the Nernstian slope of 29.5±0.5 mV per decade of Cu^{2+} concentration over a wide dynamic range (Table 1). Since the nature of plasticizer influences the dielectric constant of the membrane phase, mobility of ionophore molecules and the state of ligand[25], it was expected to play a key role in

Table 1—Effect of membrane composition on ISE response

Membrane	Carrier (mg)	PVC (mg)	Plasticizer		Additive		Slope[a] (mV per decade)
			DBP (mg)	o-NPOE (mg)	OA (mg)	NaTPB (mg)	
1	3	33	64	0	0	0	21.2 ± 2.3
2	3	33	0	64	0	0	27.7 ± 1.4
3	0	33	0	67	0	0	3.3 ± 2.3
4	1	33	0	66	0	0	17.5 ± 1.5
5	5	33	0	62	0	0	25.8 ± 1.7
6	3	33	0	63	1	0	29.1 ± 1.8
7[b]	3	33	0	63	0	1	29.5 ± 0.5

[a]Conc. range: 1.0×10^{-7} to 1.0×10^{-2} *M*.
[b]Optimum comp.

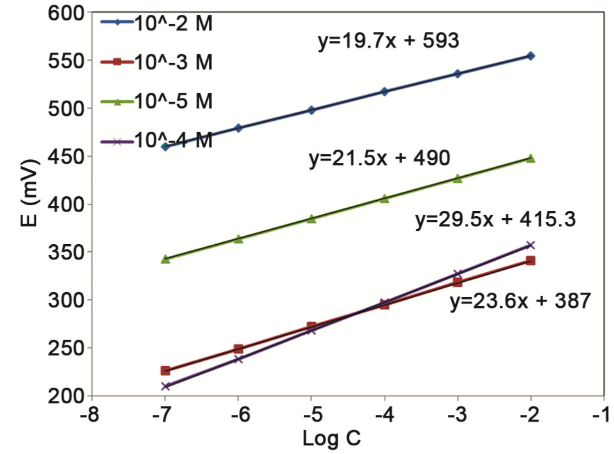

Fig. 1 — Effect of concentration of conditioning solution on potential response of membrane electrode. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

determination of the characteristics of the ion-selective electrode. As is evident from Table 1, of the two different plasticizers *o*-NPOE ($\varepsilon_r = 23.9$) and DBP ($\varepsilon_r = 6.42$) used in the preparation of the ion-selective electrodes, *o*-NPOE gave better sensitivity and wider linear range of the membrane sensor. Many studies have shown that the addition of optimum amount of ionic sites by ionic additives can improve the electrode response, selectivity and measurement range[26]. The influence of type and amount of additives was also investigated by incorporating NaTPB and OA into the membrane. Table 1 shows that membrane no. 7 with the optimal composition of 33% PVC, 63% *o*-NPOE, 1% NaTPB and 3% Schiff base results in the best sensitivity with the Nernstian slope of 29±0.5 mV per decade concentration of Cu^{2+} ions over a wide dynamic range. (For more information, please refer to the supplementary data, Figs. S2-S4).

The proposed membrane electrode was also examined with different concentrations of conditioning solution, from 1.0×10^{-2} *M* to 1.0×10^{-5} *M*. Conditioning of membrane with different concentrations of $Cu(NO_3)_2$ was found to have a very small effect on the response of the electrode potential; however in the case of 1.0×10^{-4} *M* solution, the response was more stable than with 1.0×10^{-2} *M*, 1.0×10^{-3} *M* and 1.0×10^{-5} *M* (Fig. 1). Thus, the 1.0×10^{-4} *M* solution was considered suitable for conditioning of membrane-electrode system. It should be mentioned that the stable potentials were produced by the sensor membrane at the optimal equilibrium time of 18 hours in contact with $Cu(NO_3)_2$ solutions.

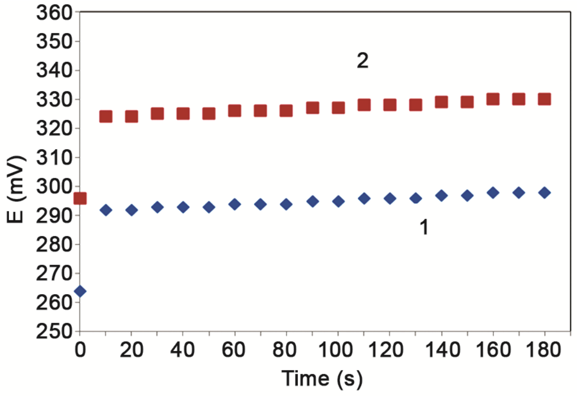

Fig. 2 — Response time of the electrode with two isolated jumps in concentration. [Curve 1: 5.0×10^{-5} *M* to 5.0×10^{-4} *M*; Curve 2: 5.0×10^{-4} *M* to 5.0×10^{-3} *M.;* Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

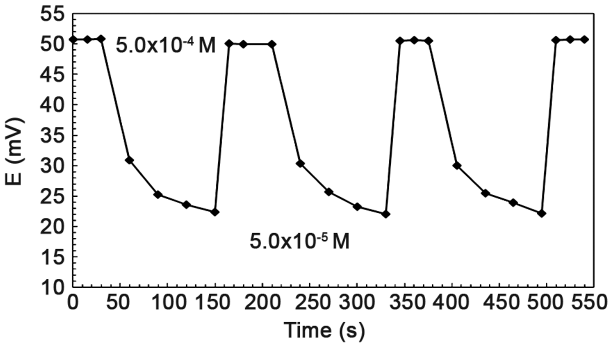

Fig. 3 — Reversibility of the copper(II)-selective electrode in several high-to-low sample cycles. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

Dynamic response time is an important factor for all ion selective electrodes. In this study, the average practical response time to achieve 90% of maximum potential after immersion in $Cu(NO_3)_2$ solutions having a 10-fold difference in concentration was recorded (Fig. 2) by two separate assessments with jumps of 5.0×10^{-5} *M* to 5.0×10^{-4} *M* and 5.0×10^{-4} *M* to 5.0×10^{-3} *M* (ref. 27). The response time was about 10 seconds and remained unchanged with different concentrations. This is probably due to the rapid exchange kinetics of complexation-decomplexation of Cu^{2+} ion with the ionophore at the test solution-membrane interface[27]. To assess the reversibility of the electrode, measurements were carried out in the sequence of high-to-low sample concentrations and the results are shown in Fig. 3. Here it can be seen that the potentiometric sensor response is reversible, although the time required for reaching equilibrium was longer for the high-to-low concentration

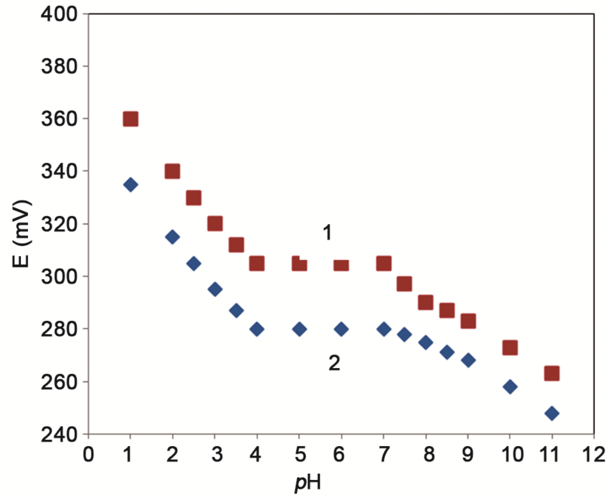

Fig. 4 — Effect of *p*H of the test solution on the potential response of the Cu^{2+} ion-selective electrode at 1.0×10^{-3} *M* (curve 1) and 1.0×10^{-4} *M* (curve 2) concentration of copper ion [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

approach. It is well proven that, in the case of the high-to-low concentration, the time required to achieve a stable potential is 100 times larger than that required for the low-to-high concentration (for 10 folds change in concentration)[27].

Effect of *p*H on the response of the membrane electrode was measured using 1.0×10^{-3} *M* and 1.0×10^{-4} *M* Cu^{2+} solution over a range of *p*H 1.0-11.0 (Fig. 4). The *p*H was set with the introduction of small drops of HCl (0.1 *M*) or NaOH (0.1 *M*). The results indicate that the potential remained stable over the *p*H range of 4.0-7.0. The drift observed at higher *p*H values may be due to the formation of Cu^{2+} ions and hydroxyl complexes in solution[28]. At low *p*Hs, H^+ ions interfere and membrane sensor responds to the hydrogen ions.

Response of the proposed sensor to different concentrations of copper(II) showed a linear behavior to the Cu^{2+} ion concentration in the range of 1.0×10^{-7} to 1.0×10^{-2} *M* (Fig. 5). The slope of the calibration curve was 29.5±0.5 mV per decade of Cu^{2+} concentration at 25.0±0.1 °C. The detection limit of the calibration curve, determined by the intersection of two extrapolated segments of calibration graph, was 7.4×10^{-8} *M* (ref. 28). The relative standard deviation of 10 replicate measurements was 0.4%. The membrane electrode can be used for at least two months without any measurable divergence.

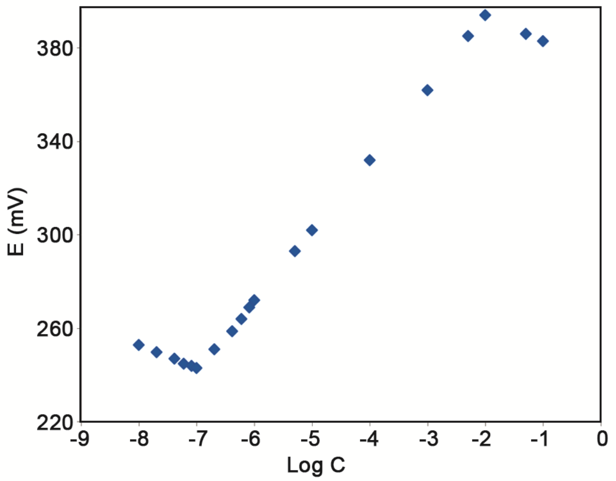

Fig. 5 — Calibration plot for the proposed ion selective electrode with optimized membrane composition. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

Table 2—Selectivity coefficient values of the proposed ion selective electrode. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%]

Metal ion	$K^{Pot.}_{Cu^{2+},J}$	Metal ion	$K^{Pot.}_{Cu^{2+},J}$
Cd^{2+}	6.53×10^{-2}	Ba^{2+}	5.44×10^{-5}
Co^{2+}	6.31×10^{-3}	Mg^{2+}	3.98×10^{-5}
Ni^{2+}	4.62×10^{-3}	NH^{4+}	1.44×10^{-5}
Zn^{2+}	3.13×10^{-3}	K^+	1.06×10^{-5}
Pb^{2+}	8.32×10^{-4}		

The most important feature of a sensor is its selectivity and represents its utility for the target sample. There are several ways to measure the coefficients of potentiometric selectivity. In this work, the values of potentiometric selectivity coefficients ($K^{Pot.}_{Cu^{2+},J}$) of the membrane were determined by the separate solution method (SSM)[29]. The resulted values for the proposed membrane are listed in Table 2. (See also supplementary data, Figs. S5-S13).

The proposed Cu^{2+} ISE based on 2-(5-bromo-2-hyroxybenzylidineamino) pyridine 3-ol was found to work well under laboratory conditions. In order to check the accuracy of the proposed method, firstly the method was used to determine copper(II) in two standard water samples as the certified reference materials, viz., CRM1643d and NIST SRM 1643e. As shown in Table 3, the observed values are in good agreement with the certified amounts and the calculated recoveries are satisfactory. From the results, it can be concluded that the proposed method is accurate and free of systematic errors. The method has also been used to analyze water samples and been validated by the samples spiked with known amounts

Table 3—Determination of Cu^{2+} from certified and sample waters. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%]

Samples	Cert. value of Cu^{2+} (*M*)	Conc. of spiked Cu^{2+} (*M*)	Calibration curve method		Standard addition method		AAS method (GF-AAS[a] or FAAS[b])	
			Recovery (%)	RSD[c] (%)	Recovery (%)	RSD[c] (%)	Recovery (%)	RSD[c] (%)
CRM1643d[a]	3.2×10^{-7}	-	97.62	2.66	99.14	1.75	100.19	2.85
NIST SRM 1643e[a]	3.6×10^{-7}	-	98.83	2.39	100.81	1.08	100.94	3.18
Water of Khoy city[b]	-	1.0×10^{-5}	81.39	0.85	98.44	0.72	100.61	0.19
Water of Tabriz city[b]	-	1.0×10^{-5}	95.85	0.83	99.63	0.76	101.59	0.17
Industrial waste water[b]	-	1.0×10^{-5}	100.47	0.87	102.19	0.73	104.18	0.15

[a] Graphite furnace-atomic absorption spectroscopy as comparative method for the certified reference samples.
[b] Flame atomic absorption spectroscopy as comparative method for the spiked water samples certified reference samples.
[c] RSDs based on five replicate determinations.

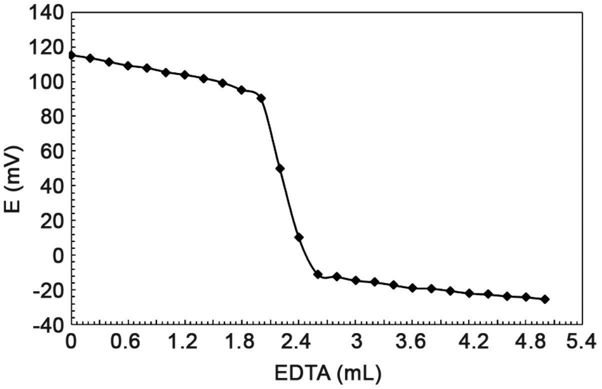

Fig. 6 — Potentiometric titration curve of 25 mL of 0.001 *M* Cu^{2+} solution with 0.01 *M* EDTA using the proposed sensor as an indicator electrode. [Membrane comp.: PVC 33% (*w/w*); Schiff base 3%; *o*-NPOE 63%; NaTPB 1%].

of copper(II). Results are found to be in a close agreement with those obtained by AAS (Table 3).

The presented copper(II)-ion selective membrane electrode was also successfully applied for the potentiometric titration of Cu^{2+} with complexing agent, ethylenediaminetetraacetic acid (EDTA). From the resulting titration curve, the amount of Cu^{2+} ions in solution was determined by the electrode (Fig. 6).

The present Schiff base has been used for the first time as ionophore. The wide linear response, non-destructive and non-contaminating, short response time, usefulness in industrial applications and being unaffected by color or turbidity are the advantages of the proposed sensor over other methods. Based on the above results, 2-(5-bromo-2-hyroxybenzylidine amino) pyridine 3-ol compound can be considered as a carrier for the construction of a novel PVC-based membrane ISE for determination of copper(II). Interference of common ions is not serious and *p*H range over which copper(II) can be measured was 4.0-7.0. The proposed electrode showed good operating characteristics (i.e. sensitivity, stability, response time, detection limit and a wide range of linearity). The optimum membrane composition was found to be: ionophore (Schiff base):PVC:*o*-NPOE:NaTPB ratio of 3:33:63:1 (*w/w*). The membrane potential response was linear in the concentration range (1.0×10^{-7} to 1.0×10^{-2} *M*) with the Nernstian slope of 29.5±0.5 mV per decade of Cu^{2+} and detection limit of 7.4×10^{-8} *M*. Response time of the electrode was very short, less than 10 seconds, and can be used for at least 8 weeks without any divergence in potential.

Supplementary data

Supplementary Data associated with this article, viz., Figs S1-S13, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(01)51-56_SupplData.pdf.

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