

Novel Copper(II)-Selective Sensor Based on a New Hexadentates Schiff's Base

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Received June 10, 2002

A novel copper(II) membrane electrode based on diphenylisocyanate bis(acetylacetonate) ethylenediimine (DIBAE), as a new hexadentates Schiff's base was prepared. The electrode exhibited a Nernstian response for Cu^{2+} ions over a wide concentration range (1.0×10^{-1} to 1.0×10^{-6} M) with a limit of detection of 6.0×10^{-7} M (39 ppb). The sensor shows a fast response time (15s) and the membrane can be used for more than 4 months without observing any major deviation. The electrode revealed very good selectivity with respect to many cations including alkali, alkaline earth, transition and heavy metal ions. The proposed sensor could be used in a pH range of 3.0-7.5. It was applied to the direct potentiometric determination of copper in black tea, and in wastewater of copper electroplating samples. The electrode was also used in potentiometric titration of the copper(II) ion with EDTA.

Key Words : Copper, Potentiometry, Hexadentates Schiff's base, Sensor, Electrode

Introduction

Carrier-based PVC membrane electrodes are now routinely used as analytical tools for the monitoring of a wide variety of different ions in various samples.¹

Due to the vital importance of copper in biological, environmental and industrial systems and the urgent need for a highly selective and sensitive copper sensor for potentiometric determination of copper in these systems, a number of potentiometric sensors based on different ionophore have reported.²⁻⁸ However, most of these copper-selective sensors suffer from the interfering effect of cations such as Zn^{2+} , Cd^{2+} , Pb^{2+} and Ag^+ .

Recently we have reported a number of sensors with sufficient selectivity and sensitivity for various ions including Hg^{2+} , Ce^{3+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Be^{2+} and Zn^{2+} .⁹⁻¹⁷ In this work we introduce a novel potentiometric sensor for selective monitoring of trace amounts of copper in various samples. The complexation ability of DIBAE was investigated for copper and some cations in non-aqueous solution by conductometric method.

Experimental Section

Materials. Reagent grade dibutyl phthalate (DBP), ortho-nitrophenyloctyl ether (NPOE), oleic acid (OA), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and used as received. The nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Doubly distilled deionized water was used throughout.

Synthesis of Hexadentates Schiff's Base. Bis(acetylacetonate) ethylenediimine (H_2BAE) was prepared as by Martell *et al.*¹⁸ ($\text{C}_6\text{H}_5\text{NHCO}$)₂ has been obtained through a method similar to that reported by Cros *et al.*¹⁹ To a solution of 4.41 g (2×10^{-2} M) of the ligand H_2BAE in 50 mL of dry acetonitrile was added 4.76 g (4×10^{-2} M) of phenyl isocyanate. The reaction mixture was stirred magnetically under reflux. After 2 h a white precipitate began to appear. The solution was stirred overnight and then concentrated. The fine material was collected by filtration and recrystallization from a benzene-hexane mixture (yield 80%)

Preparation of Membrane Electrodes. The PVC membranes were prepared according to the following general procedure. The required amounts of membrane ingredients: 30 mg PVC, 50 mg NPOE, 15 mg OA and 5 mg DIBAE was mixed and dissolved completely in 5 mL THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm in top) was dipped into the oily mixture for about 10 s, so that a non-transparent film of about 0.3 mm thickness was formed.⁹⁻¹⁷ The tube was then pulled out from the mixture and kept at room temperature about 2 h. The tube was then filled with internal filling solution (1.0×10^{-3} M copper chloride). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M solution of $\text{Cu}(\text{NO}_3)_2$. A silver-silver chloride electrode was used as an internal reference electrode.

Potential Measurements. All electromotive forces (emf) measurements were carried out with the following cell assembly:

$\text{Ag}-\text{AgCl}, 3 \text{ M KCl}, \text{internal solution } 1.0 \times 10^{-3} \text{ M CuCl}_2/\text{PVC membrane/test solution}/\text{Hg}-\text{Hg}_2\text{Cl}_2, \text{KCl (saturated)}$.

A Corning ion analyzer 250 pH meter was used for potential measurements at 25.0 ± 0.1 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled

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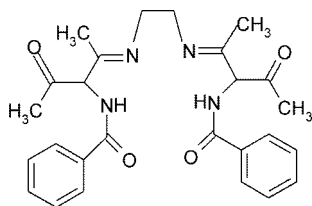
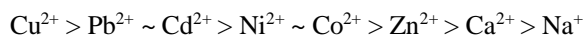


Figure 1. The structure of DIBAE.

with an ammonium nitrate solution (1.0×10^{-2}). Activities were calculated according to the Debye-Hückel procedure.²⁰

Results and Discussion

Complexation of DIBAE with Common Cations. To the best of our knowledge, there is no report on the stability of DIABE complexes with cations. Thus, the complexation of DIABE with a number of common cations was investigated conductometrically in acetonitrile solution at 25 ± 0.05 °C, in order to obtain a clue about the stability and selectivity of the resulting complexes.^{21,22} The resulting molar conductance vs. [DIABE]/[Mⁿ⁺] mole ratio plots were shown the formation of 1 : 1 complexes between DIABE and all cations that investigated. In the complex formation, all six donating atoms (four nitrogen and two oxygen atoms) are participated. The complex formation constants, K_f , were evaluated by computer fitting of the molar conductance-mole ratio data to appropriate equations,^{21,22} and the results showed that, the sequence of stability of complexes for common cations is as below:



As can be seen, it is immediately obvious that DIABE could act as a highly selective ionophore for Cu^{2+} in the membrane phase of a PVC-based ion-selective electrode.

Potential Response and Selectivity of the Electrode. In preliminary experiments the DIABE was applied as a neutral carrier to prepare PVC-membrane sensors for a wide variety of metal ions, including Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Hg^{2+} , Cs^+ , K^+ , Na^+ , Mg^{2+} and Ca^{2+} ions, and their potential responses are shown in Figure 2. As is seen, while the slopes of the linear parts of the emf responses of the sensors for all other cations shown are much lower than those expected by

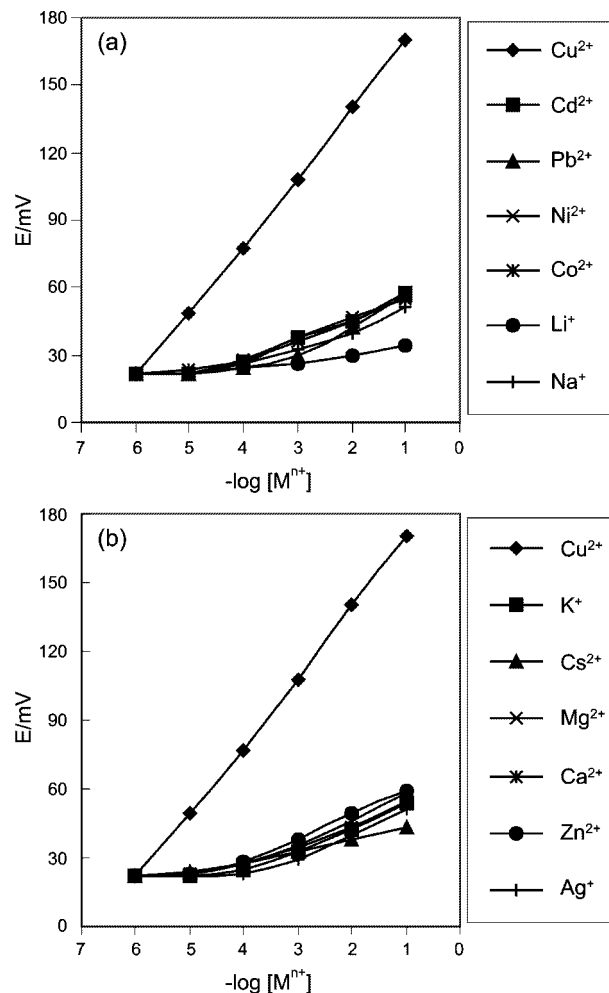


Figure 2. The potential response of various cation-selective electrodes based on DIBAE.

the Nernst equation, the resulting copper potential response is Nernstian behaviour.

Besides the critical role of the nature of ion carrier in preparing membrane-selective sensors, some other important features of the PVC membrane, such as the amount of ionophore, the nature of solvent mediator, the plasticizer/PVC ratio, and, especially, the nature of additives used, are known to significantly influence the sensitivity and selectivity.⁹⁻¹⁷ Thus, different aspects of membrane preparation based on

Table 1. Composition of PVC membranes and response characteristics of various type of Cu(II)-sensors

Electrode type	Composition/wt%				Slopes (mV/decade)	D.L. (M)
	Plastisizer	PVC	Ionophore	Additive		
1	68(DBP)	30	2	—	7.5	—
2	65(DBP)	30	5	—	10.5	—
3	63(DBP)	30	7	—	10.5	—
4	65(NPOE)	30	5	—	12.5	—
5	63(NPOE)	30	5	2(NaTPB)	29.7	7.0×10^{-7}
6	63(DBP)	30	5	2(NaTPB)	25.3	1.0×10^{-6}
7	50(NPOE)	30	5	5(OA)	25.0	1.0×10^{-6}
8	55(NPOE)	30	5	10(OA)	28.0	7.0×10^{-7}
9	50(NPOE)	30	5	15(OA)	29.8	5.0×10^{-7}

the DIABE for Cu^{2+} ion were optimised and the results are summarised in Table 1. As is obvious from Table 1 (Nos. 1-4), NPOE is a more effective solvent mediator than dibutyl phthalate in preparing the Cu^{2+} ion-selective electrode. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. The quantity of ion carrier DIABE was also found to affect the sensitivity of the membrane electrode (Nos. 8-10). The sensitivity of the electrodes response increases with increasing ionophore content until a value of 5% is reached. Further addition of ionophore will, however, result in diminished response of the electrode. This is most probably due to some inhomogenities and possible saturation of the membrane.

The data given in Table 1 reveal that the presence of additive has a beneficial influence on the performance characteristics of the membrane electrode. Addition of 15% oleic acid as a suitable additive increases the slope of the potential response of the sensor from a poor value of 12.5 mV/decade (No. 4) to a Nernstian value of 29.8 mV/decade (No. 9). The presence of anionic additives such as sodium tetraphenyl borate and oleic acid can reduce ohmic resistance and improve the response behaviour and selectivity of the membrane electrodes.^{23,24} Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface.²⁵ As is obvious, the best response characteristics are obtained with a membrane composition of 30% PVC, 55% NPOE, 5% ionophore, and 15% oleic acid (No. 9).

The influence of the concentration of internal solution on the potential response of the Cu^{2+} ion-selective electrode was studied and the results shown the variation of the concentration of the internal solution does not cause any significant difference in the potential response of the electrodes, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of internal solution is quite appropriate for smooth functioning of the electrode system.

The optimum equilibration time for the membrane sensor in the presence of 1.0×10^{-2} M $\text{Cu}(\text{NO}_3)_2$ was 24 h, after which it was found to generate stable potentials in contact with copper solutions. The average time required for the Cu^{2+} ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of copper ion solutions, each having a 10-fold difference in concentrations, was measured. The static response time thus obtained was <30 s over the entire concentration range. The sensing behaviour of the membrane sensor remained unchanged when the potentials were recorded either from low to high concentrations. The membrane electrode prepared could be used for at least 4 months without any measurable divergence.

The EMF response of the proposed Cu^{2+} sensor (prepared under optimal membrane ingredients) indicates a rectilinear range from 1.0×10^{-1} to 1.0×10^{-6} M (Fig. 2). The slope of the calibration curves was 29.8 ± 0.7 mV/decade of Cu^{2+} concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calib-

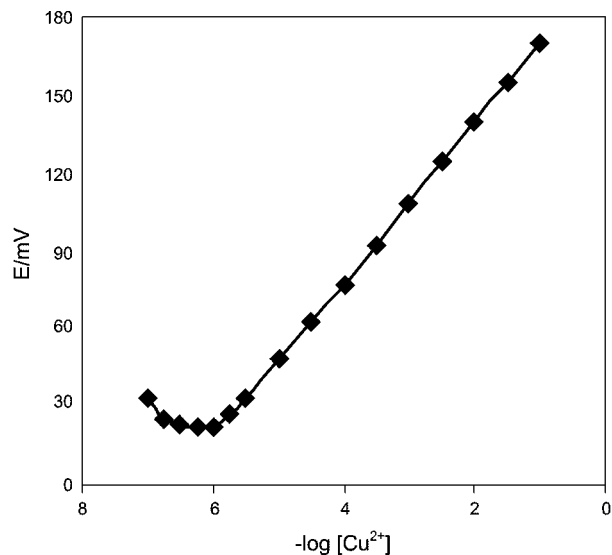


Figure 3. Calibration graph of copper(II) ion-selective electrode based on DIBAE.

ration graph, was 5.0×10^{-7} M. The standard deviation of ten replicate measurements (10^{-3} M of Cu^{2+}) was 0.5 mV.

The influence of pH on the response of the proposed membrane electrode over the pH range 2.0 to 10.0 was studied and the results are given in Figure 3. As seen, the sensor can be suitably used in the pH range 3.5-7.5. However, the observed changes below and above this pH range may be due to protonation of the Schiff's base and formation of $\text{Cu}(\text{OH})_2$, respectively.

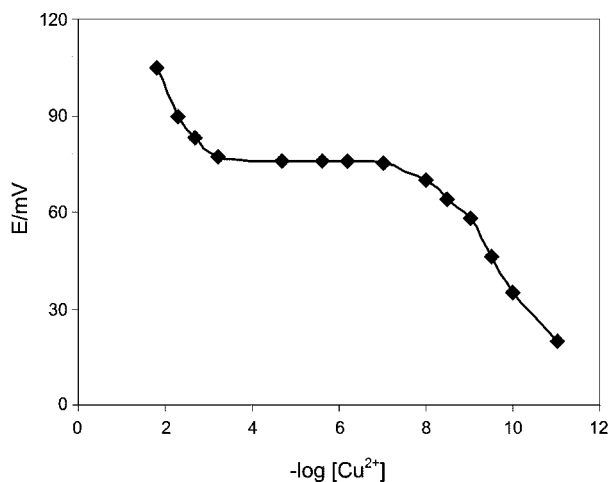
Perhaps the most important characteristic of a cation-selective membrane electrode is its relative response for the primary anion over other cations present in solution, which is usually expressed in terms of potentiometric selectivity coefficient. However, the methods based on the Nicolsky-Eisenman equation for the determination of potentiometric selectivity coefficients (*e.g.*, the fixed interference method and the mixed solution method) suffer some limitations in terms of values for ions of unequal charges, non-Nernstian behaviour of interfering ions, and activity dependence of values.²⁶ Thus, in this work, the recommended matched potential method,²⁷ which is totally independent of the Nicolsky-Eisenman equation, was used to overcome the above-stated difficulties. The resulting values are listed in Table 2. From the data given in Table 2, it is immediately obvious that the proposed $\text{Cu}(\text{II})$ sensor is highly selective with respect to the most of cations. The surprisingly high

Table 2. Selectivity coefficients of various interfering ions (M^{n+})

Ion	$K_{\text{Cu}}^{\text{Pot}}$	Ion	$K_{\text{Cu}}^{\text{Pot}}$
Li^+	4.0×10^{-5}	Ca^{2+}	4.0×10^{-4}
Na^+	1.0×10^{-4}	Co^{2+}	2.0×10^{-4}
K^+	2.0×10^{-4}	Ni^{2+}	2.0×10^{-4}
Cs^+	7.0×10^{-5}	Zn^{2+}	4.0×10^{-4}
Pb^{2+}	2.0×10^{-4}	Mg^{2+}	3.0×10^{-4}
Cd^{2+}	3.0×10^{-4}	Ag^+	1.0×10^{-4}

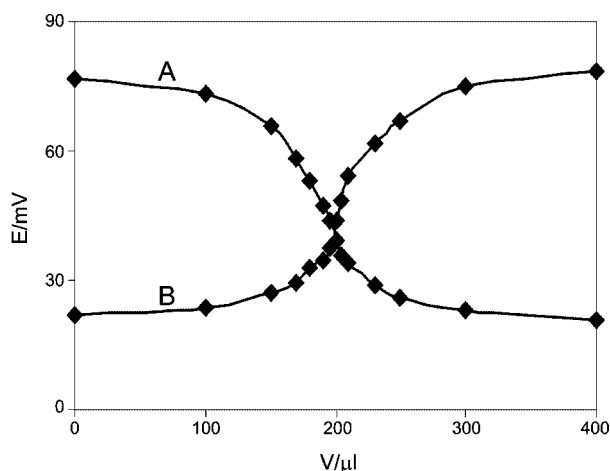
Table 3. Comparison of selectivity coefficients of different Cu²⁺ ion-selective electrodes

Ref.	Selectivity coefficients								
	Ag ⁺	Ti ⁺	Hg ²⁺	Cd ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Sr ²⁺	
2	–	–	–	2.0 × 10 ⁻³	–	5.0 × 10 ⁻⁴	1.0 × 10 ⁻²	–	
4	–	–	–	3.4 × 10 ⁻⁵	1.6 × 10 ⁻²	1.6 × 10 ⁻⁴	1.1 × 10 ⁻⁴	1.0 × 10 ⁻⁴	
5	–	–	–	4.2 × 10 ⁻⁵	1.8 × 10 ⁻¹	6.3 × 10 ⁻⁴	5.6 × 10 ⁻³	2.4 × 10 ⁻⁴	
6	–	–	–	1.0 × 10 ⁻²	6.0 × 10 ⁻²	1.0 × 10 ⁻²	1.0 × 10 ⁻³	–	
8	8.0 × 10 ⁻¹	3.0 × 10 ⁻³	1.0 × 10 ⁻²	2.0 × 10 ⁻³	2.0 × 10 ⁻³	1.0 × 10 ⁻³	1.0 × 10 ⁻³	–	
This work	1.0 × 10 ⁻⁴	–	–	3.0 × 10 ⁻⁴	2.0 × 10 ⁻⁴	2.0 × 10 ⁻⁴	4.0 × 10 ⁻⁴	–	

**Figure 4.** Effect of pH of the test solution 1.0 × 10⁻³ M of Cu²⁺ on the potential response of the Cu²⁺ ion-selective electrode.

selectivity of the membrane electrode for copper ions over other cations used most probably arises from the strong tendency of the carrier molecule for copper ions.

In the Table 3 the selectivity coefficients for the proposed sensor are compared with selectivity coefficients of previously reported PVC-membrane copper(II)-selective electrodes based on different neutral ion carriers [2,4,5,6 and 8]. As seen, the proposed electrode shows somewhat similar in

**Figure 5.** Potentiometric titration curves of 20.0 mL 1.0 × 10⁻⁴ M solution of Cu²⁺ with 1.0 × 10⁻² M of EDTA (A), and 20.0 mL 1.0 × 10⁻⁴ M solution of EDTA with 1.0 × 10⁻² M of Cu²⁺ (B).

some cases, and superior in most cases.

Analytical Application. The proposed membrane electrodes were found to work well under laboratory conditions. The sensor was used as an indicator electrode in the successful titration of Cu²⁺ with EDTA and *vice versa*. The results of both titrations are shown in Figure 5, indicating that the amount of copper ion can be accurately determined with the electrode.

It was successfully applied to the determination of copper in Iranian black tea samples. The procedure used for the extraction of copper from tea sample was similar to that reported in the literature.²⁸ One gram of the dry tea sample (dried at 110 °C) was placed in a 50 mL beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a glass watch. The beaker was allowed to stand overnight, and the contents were heated on a hot plate (150 °C for 15 min). Then the sample was cooled, 8 mL of perchloric acid was added, and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness at 150 °C. The white residue was completely dissolved in 5 mL of 1 M nitric acid and the solution was transferred to a 100 mL calibrated flask. Then, the solution was neutralized with a proper LiOH solution. Finally, 10 mL of a 0.1 M lithium acetate/acetic acid buffer solution of pH 5.5 was added and the solution was diluted to the mark. With the use of the membrane sensors calibration curve, the copper contents in the black tea samples were determined from triplicate measurements with electrode and the results are given in Table 4. As it seen, the results obtained with the sensor were found to be in satisfactory agreement with those determined by atomic absorption spectrometry.

The copper content of four wastewater of copper electroplating samples (after adjusting the pH of solution with LiOH at 5.5), was determined by the proposed electrodes using the calibration graph. The results obtained by the

Table 4. Copper content of different black tea samples

Sample	Amount of copper (ppm)	
	ISE	AAS
1 (black tea)	3.3 (± 0.2)	3.2 (± 0.1)
2 (black tea)	4.3 (± 0.4)	4.1 (± 0.1)
3 (black tea)	4.9 (± 0.4)	4.8 (± 0.2)
4 (green tea)	5.8 (± 0.3)	5.6 (± 0.1)
5 (green tea)	6.3 (± 0.4)	6.1 (± 0.1)

Table 5. Determination of copper in wastewater samples

No.	Copper found (M)	
	ISE	AAS
1	1.2×10^{-4}	1.3×10^{-4}
2	6.3×10^{-4}	6.2×10^{-4}
3	1.6×10^{-3}	1.6×10^{-3}
4	4.7×10^{-3}	4.6×10^{-3}

proposed copper sensor, together with those obtained by atomic absorption spectrometry (AAS), are summarized in Table 5. From the data given in Table 5, it is seen that there are satisfactory agreements between the results obtained by the proposed electrode sensors and those by AAS.

Conclusion

The proposed copper (II) selective membrane electrode based on diphenylisocyanate bis (acetylaceton) ethylendiamine displays a Nernstian response in a wide concentration range with a detection limit of 6.0×10^{-7} . It has a very short response time. The copper(II) electrode shows very good selectivity with respect to common cations. It can be used to determination of copper(II) in biological and industrial samples.

Acknowledgment. The authors express their appreciation to the University of Tehran Research Council for financial support of this work.

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