

A New Copper (II) Selective Membrane Sensor Based on a Binuclear Bridged Ligand

N. I. Abdullah , A. T. Numan , A.F. Hussain
Department of Chemistry, College of Education Ibn Al-Haitham, University of Baghdad

Abstract

Copper (II) ion selective PVC membrane electrode based on a bimetallic bridged complex $[\text{CuL}_2\text{Ni}(\text{en}^*)_2]$ where $\text{L} = 4\text{-oxo-1-(2H)phthalazinone}$ as a newly prepared ionophore and *o*-nitrophenyl octyl ether (*o*-NPOE) as plasticizer was prepared. The electrode exhibited a Nernstian response for Cu^{+2} ion (29.0 ± 2.0 mV/decade) over a wide concentration range ($7 \times 10^{-6} - 1.5 \times 10^{-2}$ M) with a detection limit of (2.0×10^{-6} M). The sensor showed a fast response time (30 s) and the membrane can be used for more than two months without observing any major deviation. The electrode revealed very good selectivity with respect to many cations including Na^+ , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} . The proposed sensor could be used in a pH range of 3.5 – 7.0. It was applied to the direct potentiometric determination of copper and in potentiometric titration of copper (II) ion with EDTA.

Introduction

The utility of ion selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of rapid growth of industry and technology all over the world, as they represent a rapid, accurate and low cost method of analysis. Moreover the analysis by these electrodes needs only small sample volumes. ISEs find application in various industrial and biological fields such as ion monitoring and in analysis of drinking water, food products, industrial effluents, pharmaceutical compounds etc (1-7).

Copper ion is both vital and toxic for many biological systems (8,9). The narrow window of concentration between essentiality and toxicity (10,11) warrants the determination of copper in water and biological systems. Moreover due to the increasing industrial use of copper (9), the development of new selective sensors for the determination of Cu^{2+} ion is also of special importance. So, due to this vital importance of copper in both industry and biological systems (9) and the need for a copper sensitive and selective sensor for potentiometric monitoring of Cu^{2+} ion in different samples, a variety of ion-carriers have been used to construct copper (II) selective electrodes which include crown ethers (12,13), non cyclic neutral ionophores (14-17) and Schiff bases (18,19). However, most of these copper selective sensor suffer from the interfering effect of cations such as Zn^{2+} , Cd^{2+} , Pb^{2+} and Ag^+ (16).

In this paper we have reported a highly selective copper electrode by using a binuclear complex $[\text{CuL}_2\text{Ni}(\text{en}^*)_2]$ where $[\text{L} = 4\text{-oxo-1-(2H) phthalazinone, en}^* = \text{deprotonated ethylene diamine}]$ as a neutral carrier for the potentiometric determination of trace amounts of copper ion. This complex (Figure 1) is also of interest in bioinorganic chemistry due to the importance of the structurally similar porphyrin complexes with unsymmetrical axial ligation (20,21)..

Experimental Section

Apparatus:

All potentiometric measurements were made with an Orion ion analyzer (model 701/A) using Orion type saturated calomel electrode as a reference electrode. A Phillips (PW9418) pH-meter with a glass pH electrode was used for all pH measurements. A Griffin magnetic stirrer was also used.

Reagents and solutions:

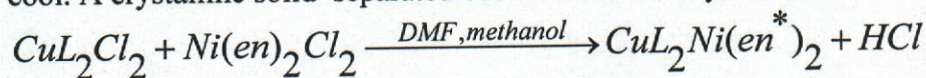
Reagent-grade *o*-nitrophenyl octyl ether (*o*-NPOE), dibutyl phthalate (DBPH), tributyl phosphate (TBP), tetrahydrofuran (THF), dimethylformamide (DMF), methanol and a high relative molecular weight PVC were purchased from Fluka and Aldrich chemical companies. Reagent-grade nitrate and chloride salts of the used cations (all from Merck and Aldrich) were used without any further purification. Doubly distilled deionized water was used throughout the work.

Stock solutions (0.1 M) of each $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , MgCl_2 , PbNO_3 , ZnCl_2 , CdNO_3 , NiCl_2 , CoCl_2 , EDTA were prepared. Other concentrations were diluted from these stock solutions.

Preparation of the complex $[\text{CuL}_2\text{Ni}(\text{en}^*)_2]$:

$[\text{Ni}(\text{en}^*)_2\text{Cl}_2]$ was prepared as by Bandini et al. (22). $[\text{CuL}_2\text{Cl}_2]$ has been obtained through a method similar to that reported by Tabassum et al. (23).

A solution of 0.635 g (0.001 M) $[\text{Ni}(\text{en}^*)_2\text{Cl}_2]$ in 20 mL of methanol was added to a solution of 0.35 g (0.001 M) $[\text{CuL}_2\text{Cl}_2]$ in 25 mL of dry dimethyl formamide (DMF). The pale green color of $[\text{CuL}_2\text{Cl}_2]$ solution changes deep green after the addition of $[\text{Ni}(\text{en}^*)_2\text{Cl}_2]$ solution. The mixture was refluxed for 2 hours, allowed to cool. A crystalline solid separated out and collected by filtration.



Electrode preparation:

0.036 g of the complex was mixed with 0.36 g of the plasticizer, 0.17 g of PVC powder and 7 mL of THF. The mixture was stirred until a clear solution was obtained. The resulting solution was then poured into a smoothed end glass casting ring (35 mm in diameter and 30 mm height) which was placed previously on a glass plate. The ring was covered with a filter paper and another glass plate, then left to allow the solution to evaporate gradually for about three days. A thin clear membrane was obtained (24).

A disk of the resulting membrane was cut and sealed to one smoothed end of a PVC tube (2.5 cm length), while the other end was connected to a glass tube containing an internal reference electrode (a wire of Ag /AgCl attached to a quickfit glass socket and immersed in a solution of 0.01 M CuCl_2 . the membrane was soaked in a standard solution of 0.1 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ overnight before using.

Results and Discussion

Ligands for use as ionophore in Cu^{2+} ion selective electrode should fulfill certain conditions. They should be selective for Cu^{2+} over other metal ions. They should have rapid exchange kinetics and

should be sufficiently lipophilic to prevent leaching of the ligand into the aqueous solution surrounding the membrane electrode. The existence of donating nitrogen atoms was expected to increase both the stability and selectivity of its copper complex. On the other hand, since the membrane components are generally dissolved in the organic polymer phase, their leaching into the sample must be kept as low as possible, the presence of benzene ring in skeleton of ligand prevents leaching of this ionophore into the aqueous solution (19).

It is well known that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition. Since the selectivity of the carrier-based ISEs are highly influenced by the membrane solvent nature (plasticizer) (25) it is expected to play a fundamental role in specifying the selective electrode characteristics. So several solvent mediators such as *o*-NPOE, DBPH, TBP which are often used in preparing PVC membrane electrodes, were evaluated and the results are summarized in the Table (1). Among these plasticizers, *o*-NPOE provided faster, more stable response with a reasonable Nernstian slope in the concentration range of $(7 \times 10^{-6} - 1.5 \times 10^{-2} \text{ mol/L})$ of Cu^{2+} .

Since the variation of the concentration of the internal solution does not cause a significant difference in the potential response of the electrode, except for an expected change in the intercept of the resulting Nernstian plots, a $(1.0 \times 10^{-2} \text{ mol/L})$ concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used as an internal solution.

The influence of pH for $1.0 \times 10^{-4} \text{ mol/L Cu}^{2+}$ on the potential response of the membrane sensor was tested in the pH range 1.0 – 9.0 and results are shown in Table (1) and Figure (3). As seen the potential remained constant from pH (3.5 – 7.0). The observed drift at lower and higher pH values could be due to the protonation of the ion carrier and of some hydroxyl complexes of Cu^{2+} ion in solution, respectively.

Optimum conditioning time for the ion selective electrode in a $1.0 \times 10^{-2} \text{ mol/L}$ copper chloride solution is 24 h (16). It then generates stable potentials when placed in contact with Cu^{2+} solution. For analytical applications according to IUPAC (26), the response time of a membrane sensor is an important factor. The static response time of the electrode, tested by measuring the average time required to achieve a potential within $\pm 1 \text{ mV}$ of the final steady-state potential upon successive immersion of a series of Cu^{2+} ion solution, each

having a tenfold difference in concentration, was within (30s) for Cu^{2+} concentrations 1.0×10^{-3} mol/L. Reproducibility of the electrode was examined by using three similar membranes under the optimum conditions. The results showed good reproducibility for the proposed electrode. For instance, the slopes observed were $(29.0 \pm 2.0 \text{ mV/decade})$ and the standard deviation of 5 identical potential measurements (at 1.0×10^{-3} mol/L) was $\pm 0.3 \text{ mV}$.

The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions and calculating the response slope. The slope of the electrode responses was reproducible over a period of at least two months. Therefore the proposed electrode can be used for 2 month without any considerable change in its response characteristics towards Cu^{2+} ion.

The potential response of the optimized electrode, to varying concentration of Cu^{2+} ions was examined and plotted on an Orion 7 cycle semi-logarithmic graph paper which is shown in Figure (2). The practical limit of detection was $(2.0 \times 10^{-6} \text{ mol/L})$ as determined from the intersection of the two extrapolated segments of the calibration graph based on the recommended procedure by IUPAC (26,27).

In addition to the Nernstian behavior, linear range and detection limit, the selectivity of the membrane sensor for Cu^{2+} ions over other metal cations is also of fundamental importance. Thus the selectivity of the membrane electrode was tested by its potential response measurements in the presence of some cations including Na^+ , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} . The selectivity coefficients, $K_{\text{Cu}^{2+}}^{\text{pot}}$ were evaluated graphically by the mixed solution method (28) from potential measurements on solutions containing a fixed concentration of Cu^{2+} ($5.0 \times 10^{-4} \text{ mol/L}$) and varying amounts of the interfering ions (M^{n+}) according to the equation :

$$K_{\text{Cu}^{2+}}^{\text{pot}} a_M^{2/n} = a_{\text{Cu}^{2+}} \{ \exp[(E_2 - E_1) F/RT] \} - a_{\text{Cu}^{2+}}$$

where E_1 and E_2 are the electrode potentials for the solution of Cu^{2+} alone and for the solution containing interfering ions as well as copper ions, respectively. The $K_{\text{Cu}^{2+}}^{\text{pot}}$ values for the diverse cations are summarized in Table (2). As can be seen for most of the diverse ions

used, the selectivity coefficients are in the order of 10^{-2} . The applicability of the proposed sensor was checked by its using as an indicator electrode for the titration of 20 mL 1.0×10^{-3} mol/L Cu^{2+} solution with 0.01 mol/L EDTA, and the result is shown in Figure (4). A very good inflection point, showing perfect stoichiometry, is observed in the titration plot. As seen the amount of copper ion in solution can be accurately determined using the electrode.

References

1. Amman, D.; Morf, W.E.; Anker, P.; Meier, P.C.; Prestsch, E. and Simon, W. (1983) Ion Selective Electrode Rev., 5, 3 – 9.
2. Janata, J.; Josowics, M.; Vanysek, P. and Devancy, D.M. (1998) Anal. Chem., 70, 179 – 185 R.
3. Buhlmann, P.; Pretsch, E. and Bakker, E. (1998) Chem. Rev., 98, 1593 – 1598.
4. Bakker, E.; Buhlmann, P.; Pretsch, E. (1997) Chem. Rev., 97, 3083 – 3090.
5. Mousavi, M.F.; Sahari, S.; Alizadeh, N. and Shamsipur, M. (2000) Anal. Chim. Acta, 414, 189 – 195.
6. Shamsipur, M.; Yousefi, M. and Ganjali, M.R. (2000) Anal. Chem. 72, 2391 – 2396.
7. Rouhollahi, A.; and Shamsipur, M. (1999) Anal. Chem., 71, 1350 – 1356.
8. Kazemi, S.Y. and Shamsipur, M. (1999) Separation and Purification Technology, 17, 181-187
9. Greenwood, N.N.; and Earnshaw, A. (1984) Chemistry of Elements, Pergamon Press, New York.
10. Fleming, C.A. and Trevors, J.T. (1989) J. Water Air Soil Pollut., 14, 143 – 148.
11. Morrison, G.M. (1995) Handbook on Metal-Ligand Interactions in Biological Fields, ed. G. Burthen, vol. 1, Chap. 7A, Marcel Dekker, New York.
12. Kamata, S.; Yamasaki, Y.; Higo, M.; Bahle, A. and Fukamaga, Y. (1988) Analyst, 113, 45 – 51.
13. Casabo, J.; Mestres, L.; Escriche, L.; Texidor, F. and Perez-Jiminez, C. (1991) J. Chem. Soc. Dalton Trans., 1969 – 1974.
14. Abbaspur, A. and Kamyabi, M.A. (2002) Anal. Chim. Acta, 455, 225 – 231.

15. Kamata, S.; Murata, H.; Kubo, Y. and Bhale, A. (1989) *Analyst*, 114, 1029 – 1036.
16. Akhond, M.; Ghaedi, M. and Tashkhourian, J. (2005) *Bull. Korean Chem. Soc.*, 26(6), 882-886
17. Ganjali, M.R.; Golmohammadi, M.; Yousefi, M.; Norouzi, P.; Salavati-Niasari, M. and Javanbakht, M. (2003) *Analytical Science*, 19, 223-227
18. Alizadeh, N.; Ershad, S.; Naeimi, H.; Sharghi, H. and Shamsipur, M. (1999) *Fresenius J. Anal. Chem.*, 365, 511 – 515.
19. Ganjali, M.R.; Emami, M. and Salavati-Niasari, M. (2002) *Bull. Korean Chem. Soc.*, 23(10), 1394-1398
20. Long, R.C. Hendrickson, D.N. (1983) *J. Am. Chem. Soc.*, 105, 1513-1521.
21. Brewer, C.T.; Bresler, G.; May, L. and Klang, J.S.R. (1993) *J. Chem. Soc. Dalton Trans.*, 1, 151-155.
22. Bandini, A.L.; Banditelli, G.; Minghetti, G. and Bonati, F. (1979) *Can. J. Chem.*, 57, 3237-3242.
23. Tabassum, S.; Singh, N.; and Arjmand, F. (2001) *Synth. React. Inorg. Met. Org. Chem.*, 31(10), 1803-1815.
24. Cragg, A.; Moody, G. J. and Thomas, J. D. R. (1974) *J. Chem. Educ.*, 51(8), 541 – 548.
25. Tavakkoli, N. and Shamsipur, M. (1996) *Anal. Lett.*, 29, 2269
26. Umezawa, Y. (1982) *Anal. Chem.*, 54, 1198 – 1205.
27. Guilbault, G.G.; Durst, R.A. and Frisier, H. (1976) *Pure Appl. Chem.*, 48, 127 – 132.
28. Bakker, E. (1997) *Electroanalysis*, 9, 7 – 13.

Electrode No.	Plasticizer	Slope (mV/decade)	Conc. Range (M)	Detection Limit (M)	Response Time (s)	Life Time (day)	R ²	pH
1	<i>o</i> -NPOE	29	7×10^{-6} - 1.5×10^{-2}	2×10^{-6}	30	60	0.9988	3.5-7.0
2	DBPH	31	2×10^{-5} - 1×10^{-2}	8×10^{-6}	50	45	0.9985	3.5-6.3
3	TBP	27.7	7×10^{-5} - 3×10^{-2}	3×10^{-5}	30	14	0.9959	3.1-6.0

Table(1): Potential Response and Other Specifications of Cu Ion Selective Electrode Using Various Plasticizers.

Interfering Ion	$K_{Cu^{2+}}^{pot}$
Na ⁺	1.5×10^{-2}
Mg ²⁺	2.3×10^{-2}
Pb ²⁺	6.8×10^{-2}
Zn ²⁺	5.0×10^{-2}
Cd ²⁺	6.9×10^{-2}
Ni ²⁺	8.4×10^{-2}
Co ²⁺	2.5×10^{-2}

Table(2): Selectivity Coefficients of Various Interfering Ions

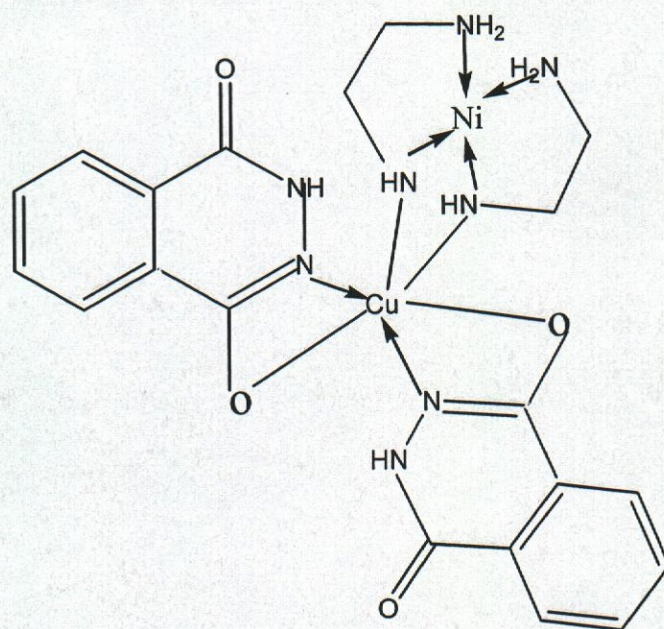
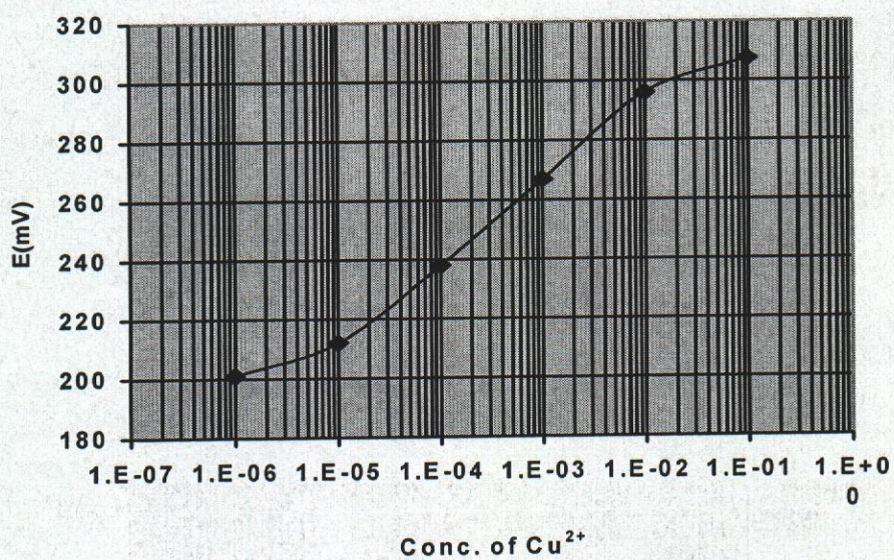


Fig.(1): Structure of the Complex

Fig.(2) Calibration Curve for the Prepared Cu^{2+} Selective Electrode Based on *o*-NPOE as Plasticizer

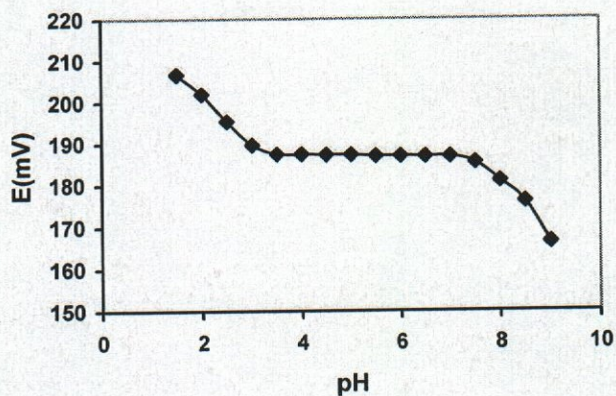


Fig.(3) Effect of pH on the Potential Response of the Copper Selective Electrode in 1×10^{-4} M Cu^{2+} Solution

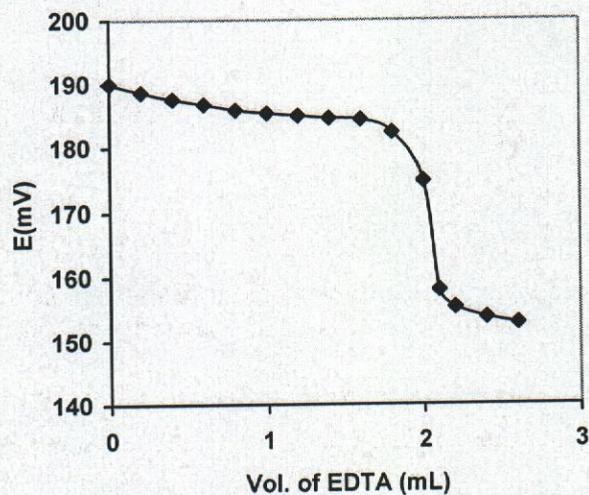


Fig.(4) Potentiometric Titration Curve of 20 mL 10^{-3} M Cu^{2+} Solution with 10^{-2} M EDTA at pH 5 using the Prepared Copper Electrode Depending on *o*-NPOE Plasticizer as an Indicator Electrode.

القطب إنتقائي الآيوني الغشائي الجديد للنحاس الثنائي المعتمد على الليكاند الجسري الثنائي النواة

نجوى إسحق عبد الله ، أحمد ثابت نعمان ، علاء فراك حسين
قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد

الخلاصة

تم تحضير قطب غشاء PVC إنتقائي آيوني للنحاس الثنائي معتمداً على المعقد الجسري الثنائي النواة المحضر الجديد $[CuL_2Ni(en^*)_2]$ كمادة فعالة، حيث $L = 4 - oxo - 1 - (2H) phthalazinone$ وباسـتخدام $o - Nitrophenyl Octyl Ether (o - NPOE)$ كمادة ملدنة.

أظهر القطب إستجابة نرنستية لأيونات النحاس الثنائية (Cu^{2+}) مقدارها $(29.0 \pm 2.0 \text{ mV/decade})$ لمدى واسع من التراكيز تراوح بين $(7 \times 10^{-6} - 1.5 \times 10^{-2} \text{ M})$ وبحد تحسس $(2.0 \times 10^{-6} \text{ M})$ وزمن إستجابة قصير (30s) وعمر زمني يزيد عن الشهرين بدون حصول إنحراف.

أبدى القطب إنتقائية جيدة بوجود العديد من الأيونات الموجبة شملت $Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Mg^{2+}, Na^+$ تراوح مدى الدالة الحامضية التي يعمل بها المتحسس بين (3.5 – 7.0).

استخدم القطب في التعيين الجهدي لأيونات النحاس باستخدام الطرائق التحليلية والتي شملت الطريقة المباشرة وطريقة التسحيح الجهدي ضد محلول EDTA.