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COPPER II-SELECTIVE MEMBRANE BASED ON A NEUTRAL CARRIER

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Resumen

Una membrana de PVC sobre la base de un electrodo-furoil-3 ,3-diethylthiourea estaba preparado para Cu^{2+} detección y determinación. El electrodo propuesto presenta un comportamiento casi nernstiana lo largo de un amplio rango de concentraciones ($1,0 \cdot 10^{-7}$ a $1,0 \cdot 10^{-2}$ mol/dm^3), con una pendiente de $29,34 \pm 0,6$ mV/dec y con un límite de detección (PDL) de $3,84 \cdot 10^{-7}$ y el límite inferior de respuesta lineal (LLLR) de $6,15 \cdot 10^{-7}$ mol/dm^3 y una vida útil de 20 días. El tiempo de respuesta dinámica y otras características de los electrodos también se estudiaron.

Palabras clave: neutro portador; de cobre del sensor potenciométrico II-selectiva; electrodo selectivo de iones (ISE).

Abstract

A PVC membrane electrode based on 1-furoyl-3,3-diethylthiourea was prepared for Cu^{2+} detection and determination. The proposed electrode exhibits a near- Nernstian behaviour over a wide concentration range ($1,0 \cdot 10^{-7}$ to $1,0 \cdot 10^{-2}$ mol/dm^3), with a slope of $29,34 \pm 0,6$ mV/dec and with a practical detection limit (PDL) of $3,84 \cdot 10^{-7}$ and lower limit of linear response (LLLR) of $6,15 \cdot 10^{-7}$ mol/dm^3 and a life-time of 20 days. The dynamic response time and other characteristics of the electrodes were also studied.

Keywords: neutral carrier; copper II-selective potentiometric sensor; ion-selective electrode (ISE).

Introduction

The presence of copper in the environment can affect the human and animal health. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. However, copper deficiency causes anemia /1/. That's why, having an efficient and fast method for the determination of this ion is necessary.

Potentiometric measurements with copper ion selective electrode allow the direct determination of free Cu^{2+} ion concentration in aqueous samples. Ion-selective electrodes (ISEs) based on ionophores are widely used /2-10/ and plasticized polyvinyl chloride (PVC) membrane ISEs based on several kinds of neutral carriers, such as Schiff's bases /2/, calixazacrown ether /3/ as typical ionophore are convenient for determining ionic species in analytical chemistry and environmental monitoring.

The present study describes polymer membrane electrodes responsive to Cu^{2+} ions based on 1-furoyl-3,3-diethylthiourea as a new neutral carrier containing chelating sites.

Experimental

Materials and methods

All the reagents used in this study were of analytical grade. Poly(vinylchloride) (PVC) from Fluka was used as polymeric matrix. The plasticizer used was dioctyl phthalate (DOP) from Riedel-de Haën and was employed as solvent mediator of the

PVC liquid membrane. Tetrahydrofurane (THF) was analytical grade from Merck. The 1-furoil-3,3-dietiltiourea was synthesized in the laboratory of natural products of the University of Havana, Cuba. The epoxy conducting resin was prepared by mixing Araldite M and Hardener H form Ciba-Geigy and graphite powder from Merck as already described by Arada Pérez *et.al.*/11/ for nitrate sensors obtaining a resistance of ≤ 2 kΩ.

The water used in this work was bidistilled water with a conductivity of less than 2 $\mu S/cm^{-1}$.

A pH/mv meter OAKLON digital pH meter with a precision of ± 0,1 mV was used for measuring the potential difference between reference and indicator electrodes. The reference electrode used in this study was an Ag/AgCl HI 5311 double junction electrode and a solution of 0,1 mol/dm^3 of K_2SO_4 was employed in the external electrode compartment. A microprocessor Hanna pH meter model 213 was used for measuring the pH with a combined electrode with epoxy body Oaklon model WD–35881–00 and a hot plate-stirrer Jenway model 1000 LT.

Preparation of the membranes

The prepared membranes contained 6 Wt. % of 1-furoyl-3,3-diethylthiourea as ionophore, 61 Wt. % of dioctyl phthalate as plasticizer and 33 Wt. % of PVC as the polymeric matrix. The preparation of the electrode were carried out in a similar manner as the method used for the construction of the all-solid-state ion selective electrodes reported in the literature /11/.

Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out by using an open cell to ambient temperature. The composition of the electrochemical cell was:

Ag/AgCl|KCl 0,1mol/dm^3|K_2SO_4 0,1mol/dm^3||test solution||PVCmemb.|cond. supp.|$Cu_{(s)}$

The calibration curves were used to calculate such parameters as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). This was done following the Nernst law through data adjustment by linear regression method. The calibration parameters were obtained by applying the method of additions /12/, determining the activity of the principal ion by using the Debye-Hückel equation (equation 1).

$$\log f = 0{,}51 Z^2 I^{1/2} / 1 + I^{1/2} \qquad (1)$$

The selectivity coefficients (K_{AB}^{Pot}) were determined by using the method of mixed solutions /12/ through the equation 2.

$$K_{AB}^{Pot} = \frac{a_A}{a_B^{Z_A Z_B}} \qquad (2)$$

● Results and discussion

The calibration parameters and other working characteristics of the ISE evaluated are shown in table 1. It is seen from this table that the constructed electrodes responded adequately to Cu^{2+} ions. Figure 1 shows the calibration curve obtained for Cu^{2+}, Cd^{2+}, Pb^{2+} ions and figure 2 shows the calibration curve obtained for Cu^{2+} ions.

As can be seen in the figure 1, the proposed electrode shows good slope nernstian by copper ions, no that way by Cd^{2+}, Pb^{2+} ions.

Their calibration curves were repeatedly obtained during life time of 20 days the electrode (n= 3).

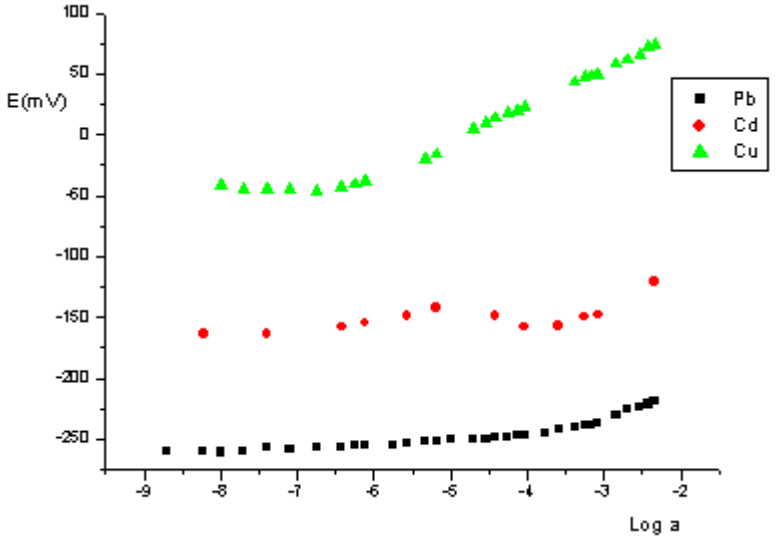

Fig. 1 Potential response of various ion selective electrode 6 Wt. % ionofore, 61 Wt. % of dioctyl phthalate and 33 Wt. % of PVC.

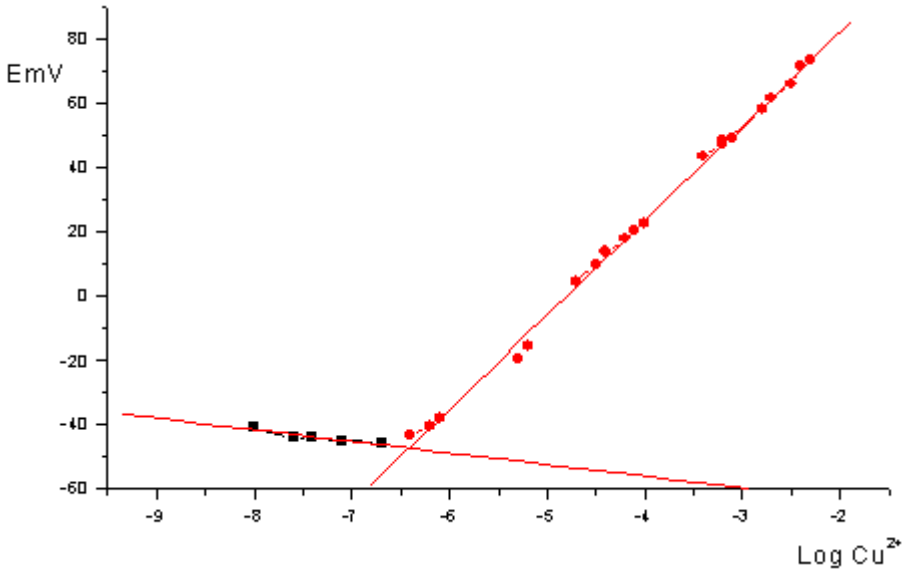

Fig. 2 Calibration curve of a copper ion selective electrode.

TABLE 1. WORKING CHARACTERISTICS OF THE ISE EVALUATED

Characteristics	
Slope (mV/dec)	29,34± 0,6
Practical limit of detection	$3{,}84 \cdot 10^{-7}$
Lower limit of linear response	$6{,}15 \cdot 10^{-7}$
Response time (s)	20
Lifetime	20 days
Working pH range	8-10
Potentiometric selectivity Coefficients (K_{AB}^{Pot})	X ($1 \cdot 10^{-2}$ mol/.dm^3) Log K_{AB}^{Pot} Ag^+ -3,1 Pb^{2+} -2,9 Cd^{2+} -3,5

Dynamic response time

The dynamic response time is an important factor for any ion selective electrode. In this study, the practical response time was registered by changing the Cu^{2+} concentration in solution over a concentration range of $4 \cdot 10^{-8}$ to $8{,}69 \cdot 10^{-3}$ mol/dm^3. The actual potential versus time traces is shown in figure 3 as can be, the concentration range the electrode reaches is equilibrium response in a short time.

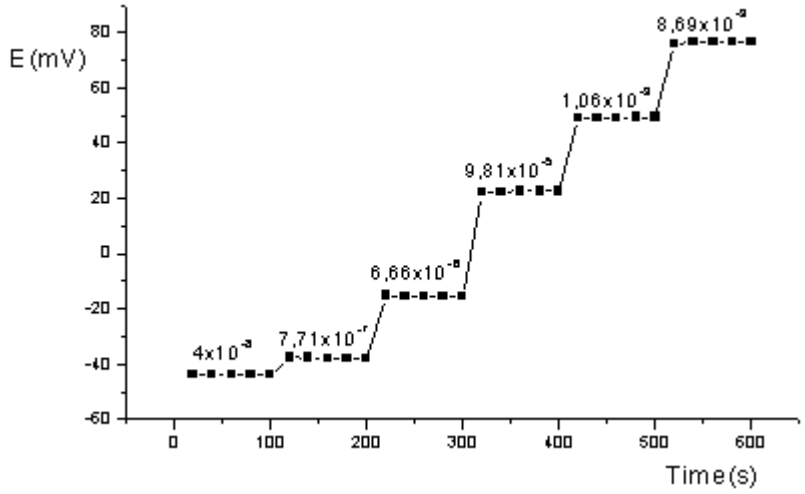

Fig. 3 Dynamic response of a Cu^{2+} membrane electrode for step changes in the concentration of Cu^{2+}.

Influence of pH on the response of the electrodes

The effect of pH on the response of the electrodes was studied in this work by using the corresponding Reilley´s diagram. An adjustment of pH was performed using dilute sodium hydroxide and nitric acid. The experimental results showed that the variation of pH affected notably the electrode potential, the electrode potential remains constant in pH intervals of 8,0 to 10,0.

Study of the effect of interfering cations on the selectivity of the constructed ISE

The influence of the presence of some ions in solution on the response of the ISEs was investigated. This is measured in terms of the potentiometric selectivity coefficient /12/ (K_{AB}^{Pot}) has been evaluated by the mixed solution method and the results are shown in table 1.

As can be seen from table 1, the Pb^{2+} presented major interference by the constructed ISE.

Conclusions

In this work, a simple and valuable ion selective electrode for Cu^{2+} was constructed by using 1-furoil-3,3-diethylthiourea as a neutral carrier (ionophore). The ISEs showed Nernstian slope for Cu^{2+} with a practical detection limit (PDL) of $3{,}84 \cdot 10^{-7}$ mol/dm^3 and a response time of 20 s. The Cu^{2+} ISE worked effectively in the pH range of 8,0–10,0 and had a lifetime of 20 days.

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