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HIGHLY SELECTIVE PVC-MEMBRANE ELECTRODES BASED ON 5-(4-DIMETHYLAMINO) BENZYLIDENE) RHODANINE FOR DETERMINATION OF SILVER ION

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● Resumen

El 5 -(4-dimetilamino) bencilideno) Rhodanine se examinó como ionóforo para la preparación de electrodos de membrana polimérica. El electrodo reveló un comportamiento nernstiana sobre la concentración de iones de Ag^+ rangos muy amplios y el límite de detección ($9{,}77 \cdot 10^{-7}$ mol /dm^3). Los electrodos de manifiesto una respuesta rápida, buena selectividad en relación con una amplia variedad de iones. El ESI propuesto puede ser utilizado por más de dos meses. Los electrodos se aplicaron a la determinación de ion Ag^+ en las muestras.

Palabras clave: electrodo selectivo de iones de plata, ftalato (DOP), 5 - (4-dimetilamino) bencilideno) Rhodanine, membranas líquidas, poli (cloruro de vinilo).

●Abstract

The 5-(4-Dimethylamino) benzylidene) Rhodanine was examined as ionophore for the preparation of polymeric membrane electrodes. The electrode revealed a Nernstian behaviour over very wide Ag^+ ion concentration ranges and detection limit ($9{,}77 \cdot 10^{-7}$ mol/dm^3). The electrodes manifest fast response, good selectivity relative to a wide variety of ions. The ESI proposed can be used for over 2 months. The electrodes were applied to the determination of Ag^+ ion in samples.

Keywords: ion-selective electrode, silver ion, dioctylphthalate (DOP), 5-(4-Dimethylamino) benzylidene) Rhodanine , liquid membranes, poly(vinyl chloride).

● Introduction

A large number of ISEs have been prepared and studied for detection of silver ion, based on crown ethers /1, 2/, macrocycles and thia macrocycles /3-5/ between others.

A variety of volumetric, espectrographic, colorimetric, polarographic techniques, and another one analytical techniques are useful for the silver determination in biological proofs and abiotic. Voltametric techniques using anodic denudation have been unrolled to measure the ion free silver in solution in concentrations like so low like 0,1 g.dm3. However, the method does not work well with natural signs that they contain big quantities of matter organic. Other methods that are used such as culombimetric, potentiometric and methods of analysis of continuous flow with the job of electrochemical detectors /6-10/.

In general, the majority the analytical techniques that are used at present in the silver quantitative determination are extremely complicated, expensive at the same level as traces and with them it works out very difficult monitoring this ion, having in account also that the silver in solution can get lost dependence of the time between the collection of the sign and analysis.

For this reason is necessary to have versatility in the methods of analysis that allow getting out results with a time reduced of analysis, low limits of detection, good selectivity, ample intervals of answer with the use of simple devices.

The selectivity coefficient is widely accepted for describing the ability of an ion selective electrode to discriminate the most relevant interfering ions from the primary analyte. In this words is employed the method of mixed solutions10, based on the Nickolsky-Eisenman equation and determined with the constructed electrode silver in solution, using he method of assessment potentiometric.

● Experimental

Materials and methods

The water used in this work was bidistilled water with a conductivity of less than 2 µS/cm^{-1}. All the reagents used in this study were of analytical grade. Poly(vinylchloride) (PVC) from Fluka was used as polymeric matrix. 5-(4-Dimethylamino) benzylidene) Rhodanine as ionophore from Merck. .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 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 for nitrate sensors /11/ obtaining a resistance of ≤ 2 kΩ.

A pH/mv/^{o}C 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 a 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, Microprocessor pH meter 213 Hanna was used for measuring the pH with a combined electrode OAKLON Epoxy boody WD – 35881 – 00 and hot plate y stirner Jenway 1000. LT

● Preparation of the membranes

The preparation of the electrode body and the application of the membrane was 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/.

The prepared membranes contained 5 % of the ionophore, 65 % of the plasticizer and 30 % of the polymeric matrix (PVC).

Determination of the electromotive force (EMF)

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

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

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 additions12, determining the activity of the principal ion by using the Debye-Hückel equation (equation 1).

$$\log f = 0{,}51Z^2I^{½}\Big/_{1} + I^{½} \qquad (1)$$

The selectivity coefficients (K_{AB}^{Pot}) were determined by using the method of mixed solutions12 through the equation 2.

$$K_{AB}^{Pot} = \frac{\alpha_A}{\alpha_B^{\,Z_A/Z_B}} \qquad (2)$$

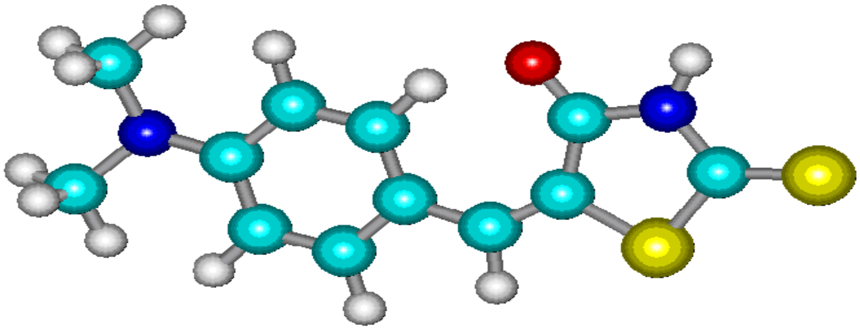

Figure 1. Structure of 1-furoil-3,3-diethylthiourea employed with ionoforo.

● Results and discussion

The parameters calibration obtained from calibration curves of electrodes are shown in table 1.

It is seen the constructed electrodes responded adequately to Ag^+. The figure 2 shows reproducibility of them answers of the ESIs to silver, by the method of additions.

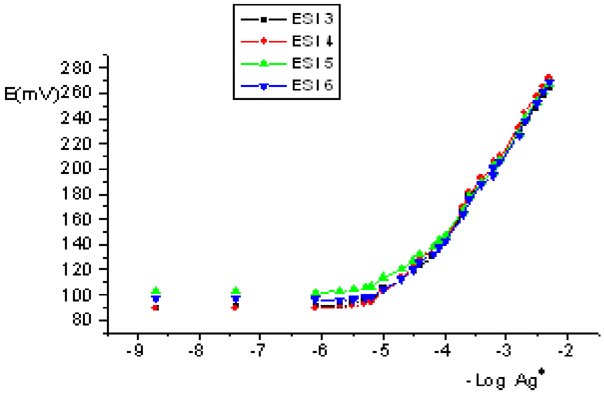

Figure2. Reproducibility of them answers of the ESIs to silver, to the 33 workdays with the ESIs.

TABLE 1: CALIBRATION PARAMETERS THE SENSOR OBTAINED

Sensor	Ag^+ (in this words)	Ag^+ ref [13]	Ag^+ ref [14]	Ag^+ ref [14]	Ag^+ ref [15]
Ionophore	**Rhodanine**	Cyclam	(MBT)	(MBI)	**calixarene**
plasticizers	DOP	DEP	DOP	DOP	**DBP**
S mV/decade	58,24 ± 0,78	59 ±2 mV	57.8	60,2	56
LPD mol/dm^3	$9{,}77 \cdot 10^{-7}$	$5 \cdot 10^{-8}$	$4 \cdot 10^{-7}$	$6{,}3\_10^{-7}$	5M
LIRL mol/dm^3	$2{,}02 \cdot 10^{-6}$	-	-	-	
$T_{rep.}$ s	20	40	10-20	10	<10 s
Sd (S):	1,03				
r	0,999 12				

where:

DOP (dioctyl phthalate)
DEP (diethyl phthalate)

DBP (dibutyl phthalate)

(calixarene): 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxybis [(2-ethylthio) ethoxy]calixarene

As can be seen from Table 1, the slope (S) correspond to those expected by Nernst for a monovalent cation (58,24 ± 0,78).The less sensible values of S correspond to sensors ref /14, 15/, constructed by using (MBT) as ionophore and (DOP) as plasticizers /14/ and (calixarene) as ionophore and (DBP) as plasticizers.

The most sensible values of S correspond to sensors ref /13, 14/, constructed by using (Cyclam) as ionophore and (DEP) as plasticizers /13/ and constructed by using (MBI) as ionophore and (DOP) as plasticizers /14/.

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 Ag^+ 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.

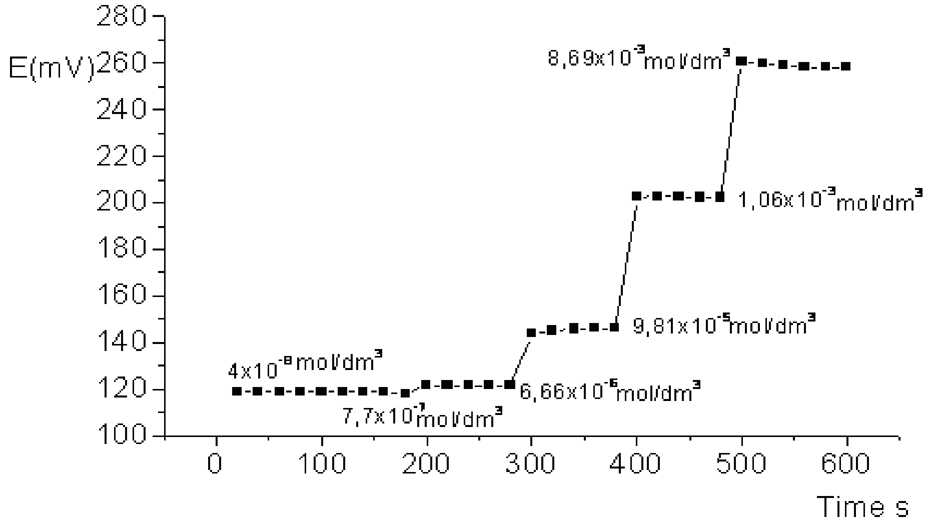

Figure3. Dynamic response of a Ag^+ membrane electrode for step changes in the concentration of Ag^+.

Study of the effect of interfering anions on the potentiometric selectivity coefficient ( )

The quantification of the selectivity of the constructed electrodes can be obtained by measuring the degree of the interference of different ions on the response of the electrode for Ag^+ ion. This was done by determination of the corresponding potentiometric selectivity coefficient ( ) in the presence of different interfering ions and the results are shown in Table 2.

TABLE 2: SELECTIVITY DETERMINED FOR THE ISE OF LIQUID MEMBRANE, USING THE MIXED SOLUTION METHOD, IN THE PRESENCE OF DIFFERENT INTERFERING IONS WITH A CONCENTRATION OF 10^{-2} mol/dm^3

Interfering ion	(in this works) K_{AB}^{Pot}	(in this works) Log K_{AB}^{Pot}	Ref[12] K_{AB}^{Pot}
Zn (II)	$7,2 \cdot 10^{-3}$	-2,14	$7,2 \cdot 10^{-3}$
Cu (II)	$3,1 \cdot 10^{-3}$	-2,50	$3,1 \cdot 10^{-3}$
Pb (II)	$1,9 \cdot 10^{-3}$	-2,70	$1,9 \cdot 10^{-3}$
Cd (II)	$1,5 \cdot 10^{-3}$	-2,82	$1,5 \cdot 10^{-3}$
Co(II)	$7,0 \cdot 10^{-3}$	-2,15	-
Ni(II)	$1,8 \cdot 10^{-1}$	-0,74	-
Na+	$9,0 \cdot 10^{-3}$	-2,04	-
K+	$3,5 \cdot 10^{-3}$	-2,45	-

In the table 2, the selectivity coefficients of some interfering cations for previously reported silver (I) sensor are compared with the proposed sensors. As can be seen from table 2, the Ni^{+2} present major interference by the ESI constructed.

As can be seen, the proposed sensor shows similar selectivity to that reported in the literature (ref[12]).

Analytical application

The practical utility of the proposed electrode was tested by its use as an indicator electrode for the titration of $AgNO_3$ with NaCl. The resulting titration curve is shown in figure 4. As can be seen, the amount of Ag^+ in solution can be accurately, determined with the electrode.

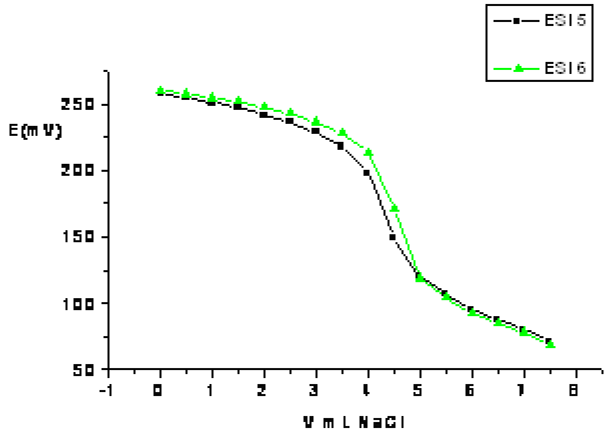

Figure 4. Potentiometric titration curves of AgNO3 with NaCl, using the proposed sensor as an indicator electrode electrode.

Conclusions

A new PVC membrane electrode selective to silver (I) was made using 5-(4-Dimethylamino) benzylidene) Rhodanine as ionophore. The prepared Ag^+ ISEs showed almost the same Nernstian slope for Ag^+ with a practical detection limit (PDL) 9,77 · 10^{-7} mol/dm^3. The prepared Ag+ ISE have a response time of 20 s and non-degradable sensor performance for 2 months.

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