

BEHAVIOR OF A POLYMERIC LIQUID MEMBRANE ION- SELECTIVE ELECTRODE FOR CHLORIDE ION

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(Received: May 15, 2013 - Accepted: July 2, 2013)

ABSTRACT

Chloride selective polymeric liquid membrane electrode has been developed by using Bis-(2-ethylhexyl) Sebacate (DOS) as plasticizer and 2-[5-(4-nitrophenyl)furyl]-4,5-diphenyl imidazole (FFDFIN) as ionophore. Some parameters of evaluation of the electrode are presented in this work. The constructed electrode showed fast potentiometric response to chloride ion in the concentration range from 10^{-6} to 10^{-2} mol.dm⁻³ with Nernstian slope of -63.43 ± 0.85 mV/decade, response time of 25 seconds and life time of 15 days.

Keywords: Chloride ion selective PVC membrane, Ion-selective electrode (ISE), 2-[5-(4-nitrophenyl)furyl]-4,5-diphenyl imidazole.

1. INTRODUCTION

The number of investigations concerning ion selective electrodes, by using various ionophores [1-4] for determination of different ions has been increasing [4-8]. These membrane electrodes are sensitive to a large number of ions. However, the number of works reported on the potentiometric determination of the chloride ion has been scarce.

The determination of the chloride ion, by potentiometric method of analysis [9-13], allows detecting and quantifying the concentration of chloride ion in a precise and exact manner. Ion selective electrodes (ISE) are very appropriate for this purpose because they are easy to build, the results are obtained quickly, they show good selectivity for inorganic ions, they are relatively of low cost and can be taken and used in the places of interest.

In this paper, we report on the use of 2-(5-(4-nitrophenyl)furyl)-4,5-diphenyl imidazole, a highly selective carrier, for detection of chloride ion using (DOS) as plasticizer in PVC polymeric liquid membrane.

2. EXPERIMENTAL

2.1 Materials and equipments

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 Bis (2-ethylhexyl) Sebacate (DOS) from Sigma-Aldrich and was employed as solvent mediator of the PVC liquid membrane. Tetrahydrofuran (THF) was analytical grade from Merck. The water used in this work was bidistilled water with a conductivity of less than $2 \mu\text{S}/\text{cm}^{-1}$. All reagents were weighed by using a Sartorius model BP analytical balance with a precision of ± 0.1 mg. A pH/mV Hanna digital with a precision of ± 0.1 mV was used for measuring the potential difference between reference and indicator electrodes. A microprocessor Hanna pH meter model 213 was used for all the pH measurements with a combined electrode with epoxy body Oaklon model WD-35881-00. The reference electrode was a double-junction Ag-AgCl containing K_2SO_4 1 mol.dm⁻³ in the other compartment. The electrochemical cell used was:

$\text{Ag}/\text{AgCl}|\text{KCl } 0.1 \text{ mol.dm}^{-3} | \text{K}_2\text{SO}_4 \text{ } 0.1 \text{ mol.dm}^{-3} || \text{test solution} || \text{PVC memb. | cond. supp. | Cu}_{(s)}$

The pH adjustments were made with dilute H_2SO_4 or NaOH solutions as required.

The ionophore was synthesized in the Polymer Laboratory of Faculty of Chemical and Pharmaceutical Sciences, University of Chile, Santiago, Chile and characterized by elemental analysis, found: C 72.77 %, H 8.74 %, N 10.17%.

2.2 Preparation of the electrode

The construction of the electrode body and deposition of the sensing membrane was carried out as shown in Figure 1.

As shown in Figure 1, the electrodes were constructed by using a 10 cm long poly(methyl methacrylate) tube (A) with a 5 mm internal diameter where a small piece of PVC tubing (2) was introduced inside to serve as support for a thin copper disk (3) which was in contact with a shielded cable (4).

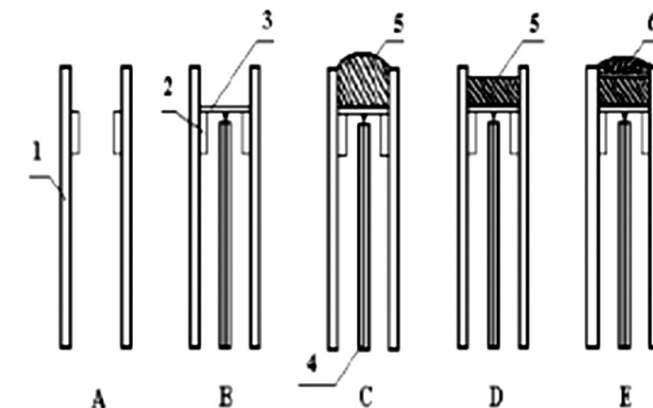


Figure 1. Construction of the all-solid-state type electrode

2.3 Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out by using an open cell at room temperature.

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

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

Where,

f is the activity coefficient of the ion to be determined, Z is its charge and I is the ionic force of the solution.

The characteristics of a membrane sensor are its response for the primary ion in the presence of the other ions. This is measured in terms of potentiometric selectivity coefficients (K_{AB}^{Pot}), which has been determined by using the method of mixed solutions [14] through the equation 2.

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

Where a_A and a_B are the activities and Z_A and Z_B are the charges of the primary ion, A, and the interfering ion, B respectively.

3. RESULTS AND DISCUSSION

Figure 2 shows that 2-(5-(4-nitrofenil)furyl)-4,5-difenil imidazole in PVC membrane is highly selective to chloride ion.

The characteristic parameters of the ISE are shown in Table 1.

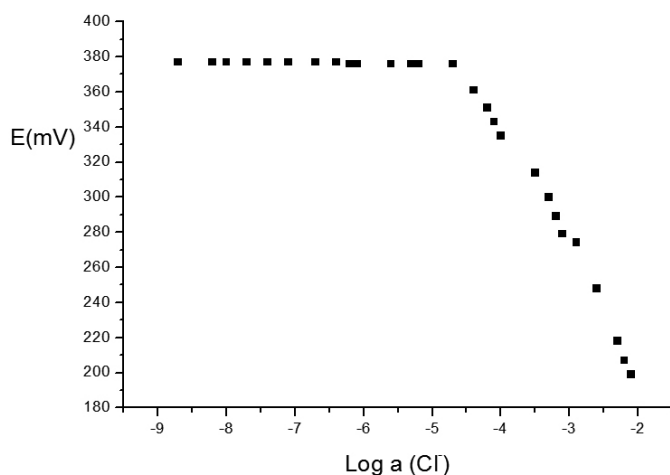


Figure 2: Calibration curve for chloride ion-selective electrode.

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 through data adjustment by linear regression method following the Nernst law.

The response of the prepared electrode was studied toward different activity of the chloride ions ranging from 10^{-9} to 10^{-2} mol.dm⁻³. The electrodes showed Nernstian slope in a wide range of the activities studied, having detection limits in order of 10^{-6} - 10^{-3} mol.dm⁻³.

The effect of the pH of the test solutions on the sensor response was studied. The potential responses indicate no significant changes at pH 2-6.

The selectivity coefficients for some interfering ions are reported in table 2, representing interferences in the determination of the primary ion.

The lifetime of the sensor was about 15 days. After this time, the electrochemical behavior of the sensor gradually deteriorates. The stability of the response time of the electrode was also studied. The static response time obtained was 25 seconds.

Table 1. Characteristic parameters for the constructed ISE.

Parameters of the calibration	
S(mV/dec)	-63.43 ± 0.8562
LPD mol.dm ⁻³	7.25 x 10 ⁻⁶
LIRL mol.dm ⁻³	1.42 x 10 ⁻⁵
Correlation coefficient	0.9989
pH	2-6
(1x 10 ⁻¹ mol.dm ⁻³ of NaCl)	15
Lifetime (days)	0.87973
SD (S)	

Table 2. Potentiometric selectivity coefficients of some interfering ions.

Ion	K_{AB}^{Pot}
NO ₃ ⁻	5.424x10 ⁻²
BrO ₃ ⁻	7.525x10 ⁻²
IO ₃ ⁻	8.75x10 ⁻²

All studied ions constitute interferences to the determination of chloride with the constructed electrode.

4. CONCLUSION

In this work a polymeric liquid membrane ion-selective electrode (ISE) for determination of chloride ion was constructed and characterized. The ion-selective electrode was prepared by using 2-(5-(4-nitrofenil)furyl)-4,5-difenil imidazole (FFDFIN) as ionophore (7 wt.-%), DOS as plasticizer (60wt.-%) and PVC as matrix (33 wt.-%). The ISE showed linear response in the concentration range of the 10^{-6} - 10^{-2} mol.dm⁻³ and with a slope of -63.43 ± 0.8562 mV/decade and a lifetime of 15 days.

ACKNOWLEDGEMENTS

María de los Ángeles Arada Pérez thanks M.Yazdani-Pedram for his collaboration.

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