Preliminary studies of PVC membranes based on 1-furoyl-3-phenylthiourea by impedance spectroscopy

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The results obtained from characterization studies of sensor membranes by impedance spectroscopy are presented in this work. The PVC membrane used contained tris(2-ethylhexyl)phosphate as a plasticizer and 1-furoyl-3-phenylthiourea as an ionophore for lead ions. To perform this study, a special cell was designed by the authors. This made it possible to study the behavior of the electrical membrane characteristics with the lead concentrations in the solution. In all cases, the shape of the impedance spectra obtained showed a clear semicircle at high frequencies. This semicircle is associated with the bulk properties of the membranes. It was not possible to resolve another semicircle corresponding to the charge transfer at the interface. For this reason our study focussed on the bulk membrane electric characteristics. Both the dependence of the membrane resistance on the solution lead ion concentration and its behavior in time are reported.

Keywords: Impedance spectroscopy; PVC membrane; chemical sensors.

En este trabajo, se presentan los resultados obtenidos del estudio de caracterización de una membrana sensora por espectroscopía de impedancias. Esta membrana se desarrolló utilizando PVC como polímero, tris(2-etilhexil)fosfato como plastificante y 1-furoil-3-feniltiourea como elemento de reconocimiento de iones plomo. Para realizar este estudio, una celda especial fue diseñada por los autores. Esto permitió el estudio del comportamiento eléctrico de la membrana para soluciones con distinta concentración de plomo. En todos los casos, en el plano de impedancias sólo fue observado un semicírculo bien definido a las altas frecuencias. Este semicírculo está asociado con las propiedades del volumen de la membrana. No fue posible resolver el otro semicírculo correspondiente a los procesos de transferencia de carga en la interfase membrana-solución. Por esta razón, sólo pudo realizarse la caracterización eléctrica del volumen de la membrana. Se reporta el comportamiento de la resistencia de la membrana con la concentración de iones plomos en la solución y el comportamiento de este mismo parámetro en el tiempo.

Descriptores: Espectroscopía de impedancias; membranas de PVC; sensores químicos.

PACS: 82.45.Rr; 82.45.Wx; 82.47.Rs; 82.80.Fk

1. Introduction

The impedance spectroscopy technique is a non-destructive and reproducible method that has become a powerful tool for characterizing the electrical properties of materials and chemical interfaces in different electrochemical processes. Recently, the impedance methods have been used to characterize Ion Selective Electrodes (ISE) and have become a useful tool for the study of ion transport through ISE membranes [1].

With the impedance spectroscopy technique, we can measure the impedance of a system (the electrochemical cell or the material to analyze) when a variable electrical signal (a known voltage or current) is applied to it. In many systems, the impedance varies as the frequency of the applied voltage changes in a way that provides valuable insights into its physical and chemical properties. After that, the principal task is to find an equivalent circuit that can give us the same experimental spectra of impedance obtained to explain the chemical and physical process of the system under study. Different authors have applied this technique to the study of ISE polymeric membranes [2-6].

Our proposal is to study, by impedance spectroscopy, polymeric membranes based on 1-furoyl-3-phenylthiourea, as a new ionophore for lead Ion Selective Electrodes. In this paper, the preliminary results of this study are presented.

2. Experimental

2.1. Materials and equipment

Tris(2-ethylhexyl)phosphate (TEHP) in Selectophore®grade, high molecular weight poly(vinyl chloride) (PVC) and tetrahydrofurane (THF) were obtained from Fluka. The ionophore for lead ions, 1-furoyl-3-phenylthiourea, was synthesized in the Institute of Materials and Reagents of Havana University. All the other salts were analytical grade (PA). Water with resistivity of 18 MΩ cm was used throughout all experiments. Platinum electrodes and wires were from Goodfellow. Impedance measurements were done using an

Analytical Impedance / Gain Phase Analyzer Solartron SI 1260, commanded by Dplot program Version 1.2.

2.2. Membrane preparation

Membranes were obtained dissolving 96.9 mg of PVC, 186.9 mg of plasticizer and 15.5 mg of ionophore in 3 ml of tetrahydrofurane. For a good homogenization of the components, the cocktail was stirred for 2 hours before being used. The membrane was left to dry for 24 hours. Precautions with the THF evaporation were taken in order to obtain a homogeneous membrane. Membrane thickness was about 66 μm.

2.3. Impedance measurements

Electrical impedance spectra were recorded at room temperature in the frequency range from 0.01 Hz to 100 kHz. The amplitude of the sinusoidal excitation signal was 200mV. The studies were carried out in the concentration range of 10^{-2} to 10^{-6} M of Pb^{2+}. Behavior of the bulk resistance in time was also recorded. All measurements were made at room temperature. A special cell, with specific characteristics for guaranteeing the characterization of the membrane, was designed and fabricated in the Institute of Microelectronics of Barcelona. The cell was made of poly(methyl mehtacrylate) and consists of two chambers, connected by a central circular orifice. The working area of the membrane was 0.38 cm^2. In both chambers, there is a platinum mesh electrode connected by a platinum wire. The electrodes are separated by a distance of 15 mm.

3. Results

In all cases studied, the shape obtained for the impedance spectra in the complex plane plot (Zreal vs Zimag) showed a clear semicircle at high frequencies (100 Hz-1 kHz). This semicircle is associated with the bulk properties of the membranes [2-6]. It was not possible to resolve the other semicircle at low frequencies corresponding to the charge transfer at the interface, because it is overlapped with the bulk semicircle. It seems to appear only in diluted solutions on the plot. For this reason our study was focussed on the bulk membrane characteristics. Bulk membrane resistance is an important characteristic related to the ion transport behavior within the membrane phase [7].

In particular, the dependence of the membrane resistance on the concentration of the bathing solution and on the time of bathing is reported.

Figure 1 shows the impedance spectra obtained for different lead concentrations in test solutions. The bulk resistance decreases with the increase of the lead concentration but, in general, the capacitance of the membrane in the high frequency semicircle remains the same at different concentrations of Pb^{2+}. The small differences in capacitance values were attributed to the different thickness obtained in the manual construction of membranes.

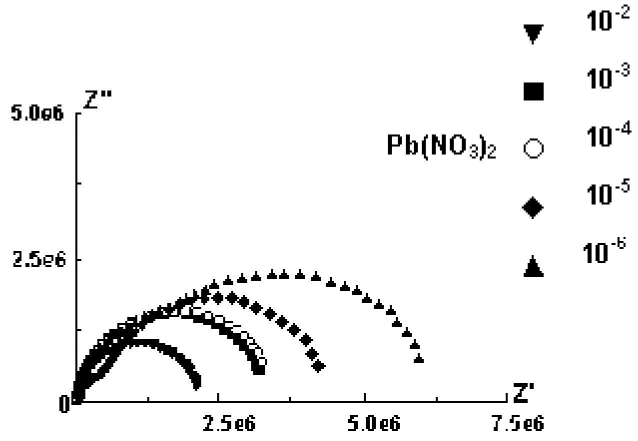

FIGURE 1. Impedance spectra (Zreal vs Zimag) of the membrane obtained at different (10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M, and 10^{-2} M) $Pb(NO_3)_2$ concentrations.

The variations of the bulk resistance showed in Fig. 1 could be associated with the diffusion of lead ions into the membrane phase from the aqueous solution.

Figures 2 and 3 show changes in the impedance spectra obtained for constant lead concentrations in time. The membrane resistance increases with the increase of soaking time at a constant lead concentration of 10^{-3} M. These variations in the bulk resistance could be associated with the membrane water uptake and with the diffusion of membrane impurities from the membrane phase to the aqueous solution. It would be necessary to study the membrane longer in order to know if this behavior would be associated with the life time of the membrane in the potentiometric mode.

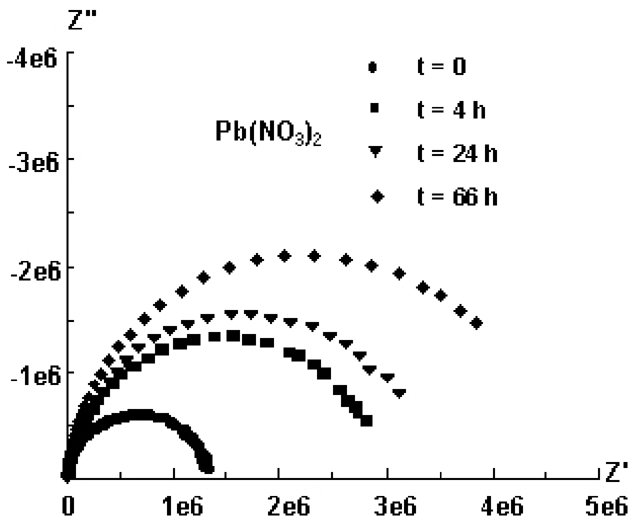

FIGURE 2. Impedance spectra (Zreal vs Zimag) of the membrane obtained at different soaking times in a fixed concentration of 10^{-3} M of $Pb(NO_3)_2$.

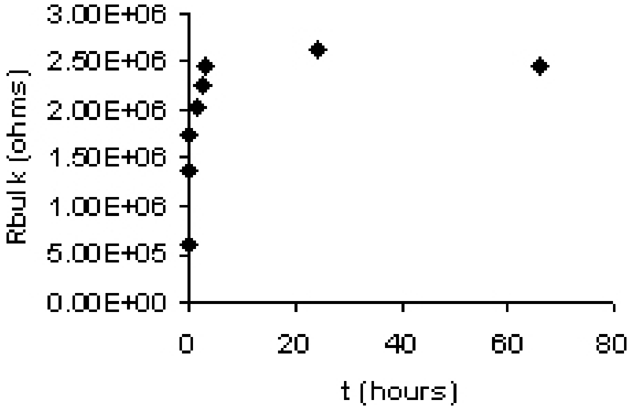

FIGURE 3. Behavior of the bulk membrane resistance in time. Membrane was immersed throughout in a bathing solution of 10^{-3} M of $Pb(NO_3)_2$.

Other authors [8,9] have found differences in the bulk resistance with soaking time, in dependence of the membrane composition, and in the characteristics of the ionophore employed.

The membrane study in this work has Nernstian response for lead ions in the potentiometric mode in the same range of concentration studied by impedance.

4. Conclusions

The impedance study of membranes based on PVC as a polymer, tris(2-ethylhexyl)phosphate as plasticizer and 1-furoyl-3-phenylthiourea as an ionophore for lead ions showed that the bulk resistance of the membrane is not constant and depends on the concentration of the lead ion that can be determined with the membrane by potentiometric measurements. Moreover, the bulk resistance also depends on the time during which the membrane was in contact with the bathing solution of this ion.

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