STUDY OF ION-SELECTIVE ELECTRODES BASED ON POLYMERIC MEMBRANES

C.Gabrielli[2], P.Hémery[1], P.Liatsi[1,2],M.Masure[1],H.Perrot[2]
1.Laboratoire de Chimie Macromoléculaire
Université Paris VI - 4, place Jussieu 75252 FRANCE
2.Physiques des Liquides et Electrochimie- UPR15 CNRS
Université Paris VI - 4, place Jussieu 75252 FRANCE

The development of efficient ion-selective electrodes has always been a big challenge for the scientists. For the fabrication of an ion selective electrode the polymer the most widely used is the PVC due to his high dielectric constant. Its rather high glass transition temperature can be reduced by addition of a plasticizer.

Membranes based on PVC with two different amounts of plasticizer (DNP) 80 and 60%, were prepared taking care to add the ionophore, an additive which imposes the membrane selectivity, and a lipophile salt conserving its electroneutrality. Two methods were used in order to characterise the polymeric membranes : potentiometry and electrochemical impedance spectroscopy.

Potentiometric measurements took place using a simple electrochemical cell with two reference electrodes. The difference of the potential established between the two membrane sides was measured with a millivoltmeter and its variation diagram was plotted versus the logarithm of the concentration. The slope was calculated and compared with the value indicated by the Nernst low. In the first case, PVC containing low quantities of plasticizer did not respond properly, meaning that the slope was much smaller than 58mV/u.log (29mV/u.log). In the other hand the PVC containing a larger amount of the same plasticizer presented a good linearity with a slope value near 58mV/u.log (fig.1). The electrochemical impedance measurements were carried out using a four-electrode electrochemical cell with two compartments separated by the membrane. The results showed (fig.2) that the quantity of the plasticizer influenced the membrane behaviour. The membrane containing 80% of DNP presented a single loop contrarily to the membrane with only 60% of plasticizer which presented a second loop at lower frequencies.

In order to explain this behaviour we developed a model that could be applied for various polymers. The PVC80DNP exhibits a good nernstian behaviour with a slope near 59mV and at the same time the presence of one loop in the impedance measurements indicates a good conductivity and so no limiting phenomena do occur. In the other hand, the PVC60DNP does not exhibit a good nernstian response and the appearance of a second loop indicates the existence of one or more limiting phenomena in the membrane/solution interface and a bad conductivity comparably to the membrane containing 80% of DNP.

Lately we have been trying to replace the PVC with other polymers having a similar structure (NBR). We thought that if the polymer has just a support role it could easily be replaced. The results we've already obtained showed that the model valid for the PVC can not be applied to all polymers as we can observe in figure 3. For different concentrations of KCl the behaviour of the membrane changes significantly. Our research is still oriented in this direction using an NBR membrane trying to understand the role of the plasticizer which maybe is the only reason for the good function of the sensor.

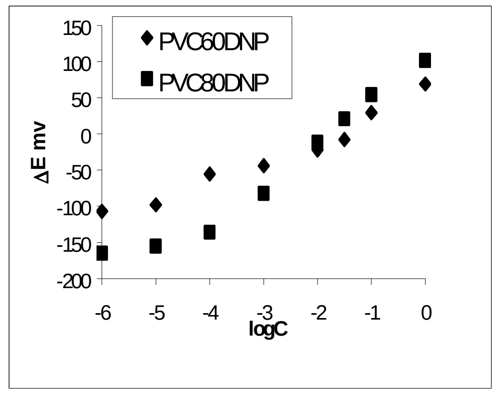

Figure 1 : Potentiometric measurements for the PVC membrane (◆) PVC60DNP slope = 27mV/u.log, (■) PVC80DNP slope 58mV/u.log.

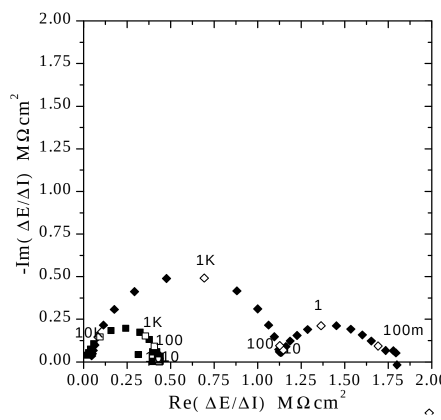

Figure 2 : Impedance measurements for the PVC membrane : (◆) PVC60DNP, (■) PVC80DNP

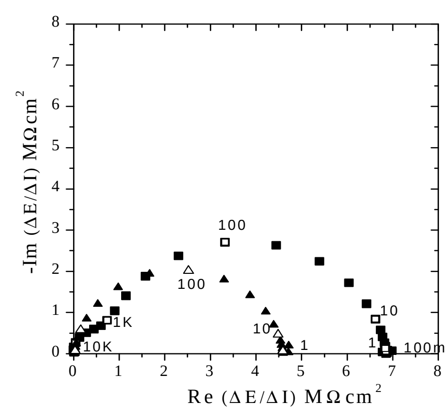

Figure 3: Impedance measurements for the NBR 50% : (◆) high concentrations (■) low concentrations of KCl

References :

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