Ion-Selective Polymeric Membranes for Chemical Sensors. I.

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Abstract – The aim of this work was to develop cation-sensors of clinical interest, i.e. potassium, calcium, magnesium sensors. Initially, new PVC based selective membranes were obtained. The potassium sensor using benzo-18-crown-6 shows a slope of 57.51 mV.dec^{-1}, while the calcium sensor using ETH 129 presents a slope of 29.11 mV.dec^{-1} and the magnesium sensor using benzo-15-crown-5 has a slope of 27.77 mV.dec^{-1}.

Keywords: chemical sensor, magnesium sensor, calcium sensor, potassium sensor, selective membrane

1 Introduction

The chemical sensors (ISFETs or ChemFETs) developed from the coupling of Ion-Selective Electrode (ISE) technology and Metal Oxide Semiconductor (MOS) technologies. In the ISFET device the gate metal of the MOSFET has been removed, an ion-selective membrane has been added to the underlying dielectric and the removed gate metal replaced by a reference electrode. On exposure of the ISFET to a solution containing the analyte for which the membrane is selective, a charge gradient is generated due to ion-exchange across the membrane/solution interface. The charge gradient, under certain conditions, can affect the current flow in the transistor. The magnitude of this current is then directly related to the charge developed, and to the activity of ions in the external solution.

This paper will present initially some aspects of ISEs, with stress on the selective electroactive membrane and its preparation. Also, considerations regarding the selective membrane behavior at its interface with the electrolyte solution are presented.

2 Ion-Selective Electrodes

An Ion-Selective Electrode is a membrane electrode, and the electric potential difference developed across it depends on the difference in ion activity in solutions on the two sides of the membrane. Such membranes could be: glasses, inorganic salts, liquid ion-exchangers, neutral carriers. The electrodes of the third and fourth categories may have their electroactive materials dispersed in polymer matrices or consist of porous diaphragms soaked with the appropriate electroactive materials.

ISEs are usually made in such way that the selective membrane is soaked on one side by a solution of constant composition consisting of the determined or primary ion and a halide ion since, often the internal reference electrode is a second kind electrode, and on the other side by a solution of the analyte whose activity is to be measured. The internal reference electrode / solution / membrane compartment provides an essentially invariant potential on the inner side of the electrode, so that the variations in potential difference across the membrane are due to the membrane / test solution ion-exchange process.

The construction of the internal reference system ensures common electrically charged particles in each phase so that the conditions of thermodynamic reversibility are realized.

3 Ion-Selective Membranes

Selective composite membranes are the active components in many selective potentiometric sensors. They have been used most successfully in contact with solutions on both sides of the membrane. In order to improve the microdevices’ life time it supposes to improve film adhesion to the solid surface [1, 2]. Such research carried out for selective membranes based on polyvinyl chloride have suggested that it is very important the understanding of the basic phenomena occurring within these membranes, referring to ions transport
in membrane, solvent adsorption and the membrane stress [3, 4].

For all potentiometric sensors, the ion-selective membrane is the key. Through various experiments has been established the preference of a sensor to respond to the ion of interest in presence of other ionic components [5, 6]. By definition, the ion-selective membrane forms a non-polarized interface with the solution containing ions of analytical interest. If the interface is permeable to only one analyte it is called "permselective" and the electrochemical potential difference is given by the Nernst equation [7]. The distinctive feature of the selective membrane is the absolute value of the total exchange current density (in general presenting a high value).

A functional, stable, reproducible and immune to the phenomena of adsorption and stirring ion-selective membrane, allows obtain high value for both the absolute current density and actual current density. For a further miniaturization, increasing importance is given to selective liquid membranes. The denomination as liquid membrane is a bit forced, because these membranes are usually solid, but this term is used especially for practical reasons [8]. These membranes are obtained by dissolving in a solvent the suitable complexing agents - ionophores. The mixture is usually set in an organic gel matrix.

As the measurements of the ionic activity takes place in aqueous medium, all the membrane constituents are hydrophobic, so that, the first interaction between the water ions and the hydrophobic membrane containing the ionophore is an extraction process [9]. In principle, such membranes could function in organic solvents, but few researches have been undertaken in this direction.

The major limitation of these membranes is the membrane solubility and / or the solvent or the ionophore extraction from the membrane. The matrix used for solvent and ionophores is high molecular weight PVC, which is typically 30% (weight parts) of the membrane [10]. Major component is the solvent (plasticizer), which provides the mobility of the free and complexed ionophore, also determining the value of dielectric constant of the membrane [11], while providing the mechanical properties of the membrane.

The ionophore, typically present in an amount of 1% (weight parts) in the membrane, corresponds to a coordinating positions of about 10⁻⁴M. Some components of the membrane include strong hydrophobic anions such as tetra phenyl borate or polysiloxanes. These components are extending the upper limit of the dynamic range by minimizing the Donnan exclusion [7].

There are two types of ionophores: some charged, which are commonly named liquid exchangers and neutral carriers, as it could be seen in Table 1 [12]. These ionophores are mobile, both in free and in complexed phase. In view of use of selective membranes as active material for ISFET's, a great importance is given to the membrane thickness. There is necessary that the total thickness must be greater than the combined thickness of the charges that lie on both sides of the membrane in order have a neutral membrane’s inside [13].

**Table 1.**

**Example of electrodes based on neutral carrier**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Membrane</th>
<th>Activ Material</th>
<th>Solvent (mediator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>Solid – PVC - siliconic rubber</td>
<td>valinomycine</td>
<td>Diociladipate</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Liquid</td>
<td>Nonactine/Monactine</td>
<td>Tris (2-ethylhexyl) phosphate</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Solid-PVC</td>
<td>ETH 1001</td>
<td>o-Nitrophenyloclyether</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>Liquid</td>
<td>Nonilphenoxi poly -(ethylene oxi)ol</td>
<td>Ba²⁺(tetraphenyl borate)</td>
</tr>
</tbody>
</table>

The thickness of spatial charge layer, \(1/\chi\), depends on the dielectric constant of the membrane and on the valence and the coordination positions concentration, being actually a Debye distance (the space where the potential or the charge drops to 1/e of their value in the linear alternative) [7]:

\[
(1/\chi) = (\varepsilon R T / 2z^2 F^2 \sum c_i)^{1/2}
\]  

(1)

where \(\varepsilon\) is the dielectric constant of the membrane, \(c_i\) - the concentration of binding positions, \(R\)-universal gas constant, \(T\) - the absolute temperature, \(z\) - valence of analyte and \(F\) is the Faraday's number.

Typically, the membrane thickness is of several thousand angstroms. In fact, the minimum thickness of polymeric membrane is of 50 µm or over, away from the value given by equation (1). Probably, this is due to the fact that these membranes are hydrated to a certain extent and develop electrical shunts. Typically, this problem does not occur with ion selective electrode operation (EIS) where relatively thick membranes - nearly 500 µm, are used. On the other hand, from the perspective of chemical sensors it is necessary to obtain membranes as thin as possible in order to assure their compatibility with the integrated circuit technology.
The response time $t$ of the membrane potential to a change in ion activity from (1) to (2) is:

$$\Delta \tau = \frac{RT}{F} \ln \left\{1 - \left[1 - \left(\frac{a_{i(1)}}{a_{i(2)}}\right)\right] e^\left(-\frac{t}{\tau}\right) \right\}$$  \hspace{1cm} (2)

where: $R$ - universal gas constant, $T$ - absolute temperature, $F$ - Faraday's number, $\tau$ - while undergoing measurement, $t$ - response time of membrane potential with changes in ion activity from (1) to (2).

The time constant value falls in a range between 30 $\mu$s (for a AgBr membrane) and 200 ms (for pH glass electrode) [7]. Because of some associated processes’ time constants, such as for the diffusion through a stagnant layer of solution or the response time of the electronics, you can record ISE’s response times of few seconds. Numerous studies on selective membrane systems have been rewarded by promotion of some higher selectivity characteristics, minimum response time and other improved properties [14-17], in order to achieve workable and robust sensors.

### 4 Interface Membrane / Aqueous Solution

Generally, in a first approximation, a membrane is considered to be homogeneous. It is therefore expected that the interface water / polymer have the associated characteristics with other liquid / liquid interfaces like interface nitrobenzene / water. Therefore, the ions present in the aqueous interface must be balanced by an equal number of charges in the opposite polymeric interface. The thermal diffusion could cause the diffusion of the charged layers. Also, it could exist an inner layer without ions, which could separate the two space regions charged.

In most cases, the concentration of ions in the aqueous phase is significantly higher than in the polymeric phase, so that the thickness of the spatial charge in polymeric phase is probably higher than in the aqueous phase. Experimentally, it was shown that for a concentration of $10^{-3}$ M electrolyte in PVC polymer (33%) - dioctyl sebacate (DOS) the Debye thickness is 3 nm, while in water the value of Debye thickness is 1 nm [19]. In the case of the membranes based on plasticized PVC with a thickness of 0.2 mm, the charged spatial region extends only over a very small distance inside the membrane (a few tens of nm).

Between the liquid / liquid interface and polymer / water interface is still a significant difference because in the polymer case, either the polymer itself or its plasticizers, can accumulate at the interface, so that interfacial composition is different from the volume composition. In addition, the existing impurities in the polymer can accumulate at the interface.

The electrolyte equilibrium distribution between the membrane and aqueous phase is realized sometimes different than it would be expected. As mentioned above, the hydrophilic salts are not removed from the membrane into the aqueous solution. Moreover, the water penetrates the membrane and it solvates "in situ" the salts.

The ionophores and plasticizers can be eliminated very slowly in aqueous solution, the process determining and limiting the life time of the electrode. The elimination of neutral substances in aqueous electrolyte, is an exudation process, which cannot be precisely controlled. This process can be followed and put in evidence using impedance measurements. By performing experiments on the surfactants exudation were found that the exudation rate may depend on the availability of the cross-adsorption positions. However, there are substances such as tetra phenyl borate, which are distributed in the membrane as in a homogeneous liquid phase. Adsorption can be virtually absent or without any influence on rates transfer.

### 5 Casting of polyvinyl chloride (PVC) Membranes

As specified above, the heterogeneous membrane sensors have electroactive material dispersed in a matrix support. Ideally, such support should be: chemically inert, hydrophobic, resilient, flexible and non-porous. The choice of solvent is also important because it could function as a plasticizer for the polymeric matrix, creating flexibility so as not to hinder conformational equilibrium, but not polar enough to respond to ions in solution. Polyvinyl chloride has been widely used as polymeric matrix, although it is by no means totally inert nor totally hydrophobic [20].

A master membrane was cast from PVC / plasticizer / electroactive material solution in tetrahydrofuran in a Teflon pot. After drying for 48 h in desiccator from this master membrane discs were cut with a cork borer. The cut membranes were mounted in a Philips electrode body to obtain the ISE.

### 6 Experimental

Magnesium, calcium and potassium – responsive PVC devices were obtained by casting doped films from tetrahydrofuran (THF) solution over a PTFE
support. The following chemicals were used for preparing the PVC selective solutions: PVC high molecular weight - Fluka, nonactin - Fluka, o-nitro phenyl octyl ether (o-NOPE) – Fluka, potassium tetra phenyl borate – Fluka, tetrahydrofuran (THF) – Fluka. As electroactive materials there were used: benzo-15-crown-5 (Sigma), benzo-18-crown-6 (Sigma) and calcium ionophore ETH 129 (Fluka).

As the previous works proved that the purity of THF used as PVC solvent affected the sensor response-time and detection limit, then freshly double-distilled THF was used exclusively [21].

ISEs were conditioned for 48 h in analyte solution (10^-2 mol.L^-1) and the measurements were performed using a series of calibration solutions of analyte (Analar grade), ranging between 10^-1 mol.L^-1 and 10^-5 mol.L^-1. All tests were carried out at constant temperature, 25°C.

After leaving the selective membranes for 24 h in desiccator for drying, the ISEs were obtained by mounting the cut membranes into a Philips electrode body. The membranes were conditioned over 24h with 10^-2 mol.L^-1 analyte chloride internal solution. The calibration solutions were made using the chloride analyte salt (Fluka) in deionised water. A double junction calomel reference electrode (Russell) was used in the performed studies. The measurements were done by help of a Cyberscan PCD 6500 from Eutech Instruments.

7 Results and Discussions

The obtained ISEs were calibrated with correspondent calibration solutions as mentioned above.

The PVC based potassium - ISE was calibrated using potassium chloride solutions. A 10^-1 mol.L^-1 potassium chloride solution was diluted using the constant volume dilution method (CVD).

In Fig.1 is presented the calibration curve for the potassium selective electrode. It could be noticed the Nernstian behavior of the potassium – ISE and the linear range between concentrations 10^-1 mol.L^-1 and 10^-4 mol.L^-1.

It has to be mentioned that the lifetime of this device was of 15 working days.

![Fig. 1. Calibration curve for potassium selective electrode](image)

A Nernstian response of 57.51 mV.dec^-1 was calibrated for the potassium ISE.

Before testing, the Mg^{2+} - ISE and Ca^{2+} - ISE were stored for 24 hours in 10^-2 mol.L^-1 MgCl_2 solution and 10^-2 mol.L^-1 CaCl_2 solution, respectively, as usual practice for commercially available liquid-filled electrodes [21, 22]. The response characteristics for the selective devices are summarized in Table 2.

<table>
<thead>
<tr>
<th>Device function</th>
<th>Analyte</th>
<th>Analyte</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response (mV/decade)</td>
<td>57.51</td>
<td>29.11</td>
<td>27.77</td>
</tr>
<tr>
<td>Range* (mol.L^-1)</td>
<td>10^-1 – 10^-4</td>
<td>10^-2 – 10^-5</td>
<td>10^-1 – 10^-4</td>
</tr>
<tr>
<td>Detection limit (mol.L^-1)</td>
<td>10^-2</td>
<td>10^-3</td>
<td>5.10^-2</td>
</tr>
<tr>
<td>95% response time (s)</td>
<td>45</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>Useful lifetime (days)</td>
<td>15</td>
<td>20</td>
<td>11</td>
</tr>
</tbody>
</table>

* Range over which devices were tested and produced a near – Nernstian response; the range is likely to extend to higher values of activity

8 Conclusion

Rapid and reproducible analysis using ISEs based on crown ethers as selective material for selective PVC membranes is possible. The obtained devices shown to offer alternative solution, capable of satisfying the increasing demand for precise analytical information at lower cost through relatively simple instrumentation.
References:


