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Mg(II) ion-selective electrode based on chlorophyll as ion exchanger

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ABSTRACT

A novel Mg(II)-responsive electrode has been constructed based on incorporation of the naturally occurring magnesium-containing chelate, chlorophyll, in a PVC membrane plasticized with dioctylphthalate. The sensor exhibited average slope of 31.2mV/Mg concentration decade over a concentration range of 4.0×10^{-5} - 2.8×10^{-2} M. The performance of the electrode was not affected by the change in pH within the range 3.9-8.4. It showed high selectivity for Mg(II) over Ca(II) and the other physiological cations, Na⁺ and K⁺. However Li⁺ was found to interfere. X-ray photoelectron spectroscopy has been applied to examine the leaching of the active ingredients from the gel layer to the bathing solution during soaking of the electrode. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

In all types of ion-selective electrodes, an interface membrane is constituted at the separation of two immiscible media. Thus, it appears that the gel layer formed at the membrane surface of the electrode acts as a transition entity between the media it separates. Inside this layer a phase exchange occurs resulting in a potential difference that is corresponding, from a thermodynamic point of view, to the change of activity of the targeted species. This phase exchange for metal cations requires either lipophilic ion-exchanger or an ionophore to host the cation. Supramolecular receptors proved to be excellent ionophores for the construction of selective sensors for several cations including magnesium^[1-11]. The function of such sensors is based on ionic recognition process followed by potential signal transduction. It is interesting that there is a similarity between the nervous cell membrane, as a natural membrane, and the ion-selective liquid membranes as artificial one^[12].

Although many of the sensors based on synthetic compounds proved high sensitivity and selectivity, al-

most all of them require manipulation of sophisticated organic chemistry schemes to prepare the ion carrier in addition to the high cost of the process.

In nature there are many naturally occurring substances that satisfy perfectly all the requirements to be employed as exchangers in ion-selective electrodes. There are good reasons to prospect that these substances would be highly selective ionophores for certain cations as they are in nature. Recently fluoride ion-selective electrode has been successfully constructed based on Al(III) porphyrins as ionophores^[13]. The electrode exhibited enhanced potentiometric selectivity for fluoride over more lipophilic anions, including perchlorate and thiocyanate. However, such membrane electrode displayed undesirable super-Nernstian behavior.

Chlorophyll is a natural substance, its chemical structure contains a ring system similar to that of porphyrin but includes a cyclopentanone ring, and one of its pyrrole rings is partially reduced. The metal in chlorophyll is magnesium.

The present article addresses the employment of chlorophyll as ion-exchanger for the construction of

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Mg²⁺-selective electrode. Beside being widely abundant, easily to be extracted, prospective as Mg(II)-exchanger from structural point of view, chlorophyll is environmentally friendly. So the work can be considered as a contribution to the green chemistry field. Moreover the proposed electrode can be used for biomedical investigation as magnesium ion is pivotal in the transfer, storage and utilization of energy; it also regulates and catalyzes some 300-odd enzyme systems in mammals. It has numerous physiological roles, among which are control of neuronal activity, cardiac excitability, neuromuscular transmission, muscular contraction, vasomotor tone, blood pressure and peripheral blood flow^[14].

The present work also aims at finding out the cause of the limitation of life span of plastic membrane ion selective electrodes. Therefore X-ray photoelectron spectroscopy has been applied to analyze the surface of an expired electrode in comparison to a fresh one.

EXPERIMENTAL

Reagents and solutions

Double distilled water and analytical grade reagents were used to prepare all solutions. Poly(vinyl chloride) (PVC) of high molecular weight and dioctylphthalate were provided by Fluka.

Preparation of the coating solution

Chlorophyll was extracted with tetrahydrofuran on cold by grinding 4.0g of fresh green leaves, collected from *Conocarpus-Lancifolia* trees, and ground in a blinder for three minutes, with two 20mL aliquots of tetrahydrofuran and filtering the extract into 100mL beaker. In the extract were dissolved 400mg of each of PVC and DOP.

Construction of the electrode

A silver rod of 10 cm length and 5.0mm diameter was tightly insulated by polyethylene tube leaving 1.0cm at one end for coating and 0.5cm at the other end for connection. The 1.0cm terminal was electrolytically coated with AgCl. The coating was carried out in 0.1M NaCl solution with the silver rod as the anode and a platinum electrode of 1.0cm² surface area as the cathode. The coating time was 10 minutes with current den-

sity of about 10mA/cm². The terminal of Ag/AgCl rod was coated with the plastic membrane by quickly dipping it into the chlorophyll-containing coating solution several times and allowing the film left on the wire to dry in air for about one minute. The process was repeated several times until a plastic membrane of proper thickness is formed. The prepared electrode was pre-conditioned by soaking it for 24hr in 1.0×10⁻⁵M solution of MgCl₂.

Potentiometric studies and electrochemical systems

Potentiometric measurements were carried out with an Orion, Model 420A pH/mV meter. The following electrochemical system was employed:

Ag/AgCl reference electrode/MgCl₂ test solution/Plastic membrane/AgCl/Ag

Construction of the calibration graphs

Suitable increments of standard MgCl₂ solution were added to 50mL of a 10⁻⁶M in MgCl₂ solution so as to cover the Mg(II) concentration range 10⁻⁶ to 5.0×10⁻²M. In this solution the sensor and the reference electrode were immersed and the emf was recorded after 10 s, at 25°C, for each addition.

Selectivity

The selectivity coefficients of the Mg-selective electrode, ($K_{Mg,J}^{pot}$) towards different cationic species J^{z+} were determined by the separate solution method (SSM)^[15].

X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded on a model VG ESCALAB 200(UK) spectrometer using MgK α radiation(1253.6eV) operating at 300W(15kV, 20mA). The spectra acquisition and processing were carried out by means of an Eclipse V 2.1 data system(UK). The plastic membrane sample was introduced into the preparation chamber with the sample holder and degassed until good vacuum achieved, then it was transferred into the analysis chamber where the pressure is reduced to 10⁻⁹10⁻¹⁰ torr. The analyses were carried out with the parameters: step size 0.1eV, Dwell time 100ms, and pass energy of 20eV. All binding energy values were determined with respect to C1s line (284.6eV) originating from adventitious carbon. Depth profiling was done with an Ar ion gun with 5 kV energy

and 1 μ A current.

To study the effect of prolonged soaking on the chlorophyll content in the gel layer of the membrane, two replicate coating mixtures were prepared as described above. Each mixture was poured into a petri dish of 7.5 diameter, and left to dry overnight. One of the two green plastic membranes formed in the petri dishes was taken out and its surface analyzed by XPS for Mg 1s, Mg 2p, O 1s, N 1s, C 1s and Cl 2p photoelectrons. The second petri dish was filled with 10^{-5} M MgCl₂ and kept in a closed vessel for 35 days. The soaking solution was then poured off and the membrane surface was washed thoroughly with distilled water. After being dried in a desiccator under vacuum, the surface of the membrane was analyzed by XPS as for the first membrane.

RESULTS AND DISCUSSION

Extraction of chlorophyll

Four replicate extraction process of chlorophyll resulted in obtaining average amount of chlorophyll equals to 0.0973g. The method was highly reproducible as the results showed coefficient of variation amounting to 2.55%. This reveals that the composition of the prepared membrane is 10.8% chlorophyll, 44.6% PVC and 44.6% (w/w) plasticizer.

Response and life-time of the electrode.

Calibration plots (pMg vs. E, mV) were obtained after continuously soaking the electrode in 1.0×10^{-5} M MgCl₂ for 24, 36 and 48h, 7, 14, 21, 28 and 35 days. The average slope was 31.2mV/Mg concentration decade over the first 48hrs and remained almost constant for the first 7 days then decreased gradually reaching 28.3, 26.1, and 21.5mV/ Mg concentration decade after 14, 21 and 28 days, respectively. The slope went down 20 mV/concentration decade after 35 days of continuous soaking indicating that the exchange process at the interfacial junction containing the gel layer is no longer efficient and that the electrode has become expired.

Effect of pH

The effect of pH of the MgCl₂ solution test solution on the electrode potential is graphically represented in figure 1. The pH of 5.0×10^{-4} M MgCl₂ solution is al-

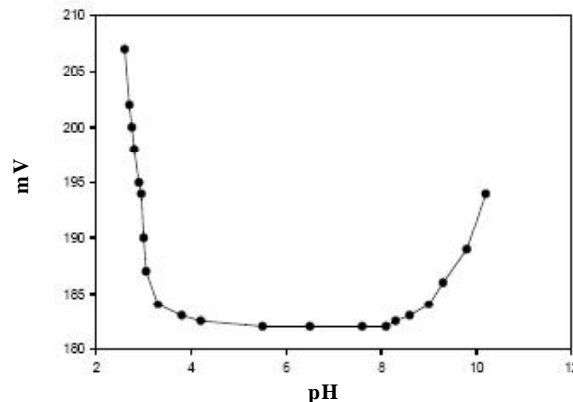


Figure 1 : Effect of pH on the response of the chlorophyll-based electrode

TABLE 1 : Selectivity coefficients ($K_{Mg,J}^{pot}$) of the Mg(II)-ion selective electrode

| Interferent J^{z+} | $K_{Mg,J}^{pot}$ | Interferent J^{z+} | $K_{Mg,J}^{pot}$ |
|----------------------|-----------------------|----------------------|-----------------------|
| Li ⁺ | 6.91×10^{-1} | Co ²⁺ | 1.86×10^{-2} |
| Na ⁺ | 7.08×10^{-3} | Ni ²⁺ | 1.56×10^{-3} |
| K ⁺ | 1.99×10^{-3} | Cu ²⁺ | 3.07×10^{-3} |
| Ca ²⁺ | 1.10×10^{-3} | Zn ²⁺ | 2.11×10^{-2} |
| Ba ²⁺ | 5.89×10^{-3} | Fe ³⁺ | 4.39×10^{-2} |
| Mn ²⁺ | 1.25×10^{-3} | | |

tered by the addition of small volumes of HCl and NaOH (0.1-1.0M each) and the potential is reported as a function of pH. From the curve, it is clear that the electrode potential showed stability in the pH-range 3.9-8.4. Below and above this region the electrode potential increased and the curve as a whole had a U shape (Figure 1). The increase in potential below pH 3.9 may be attributed to the transformation of chlorophyll to the acid form where hydronium ion phase exchange replaces the magnesium exchange at the membrane surface. On the other hand, the increase of potential at pH values greater than 8.4 is, most probably, due to penetration of sodium ions into the membrane surface.

Selectivity of the electrode

The major challenge in the design of Mg²⁺ ionophores has been for many applications in the discrimination of Ca²⁺. The values of the selectivity coefficients ($K_{Mg,J}^{pot}$) presented in TABLE 1 clearly showed that the present electrode exhibited distinguished selectivity for Mg(II) towards Ca²⁺ and many other cations including the physiological cations Na⁺ and K⁺. Nevertheless, the results also reflect high interference of Li⁺ ($K_{Mg,Li}^{pot} = 6.91 \times 10^{-1}$) which may be attributed to the fact that

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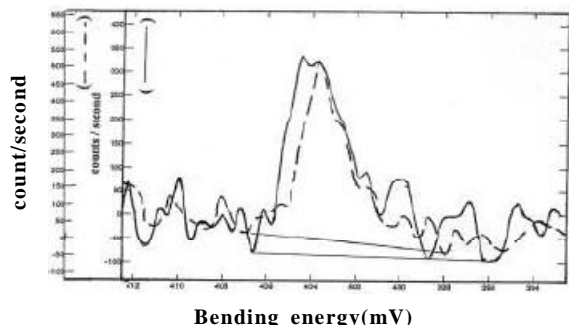


Figure 2 : X-ray photoelectron spectra of fresh (—) and expired (----) membranes

TABLE 2 : Quantification of X-ray photoelectron spectra of the surface layers of fresh and expired Mg(II) ion-selective electrodes based on chlorophyll as ion-exchanger

| Energy level | Binding energy center mV | SF* | (Fresh) Normalized peak area (counts) | Atomic % | (Expired) Normalized peak area | Atomic % |
|--------------|--------------------------|------|---------------------------------------|----------|--------------------------------|----------|
| Mg 1s | 1306.7 | 11.8 | 26.85 | 1.34 | 19.14 | 1.73 |
| O 1s | 534.5 | 2.93 | 472.33 | 23.64 | 253.93 | 22.92 |
| N 1s | 403.8 | 1.80 | 13.76 | 0.69 | 10.21 | 0.92 |
| C 1s | 286.8 | 1.00 | 1449.23 | 72.53 | 797.37 | 71.98 |
| Cl 2p | 202.00 | 2.29 | 29.74 | 1.49 | 21.61 | 1.95 |
| Mg 2p | 51.9 | 0.33 | 6.15 | 0.31 | 5.58 | 0.50 |

*Statistical factor

the two ions have close ionic radii^[16].

X-ray photoelectron spectra of the membranes

The surfaces of two membranes were investigated by X-ray photoelectron spectroscopy. One membrane was freshly prepared while the second was an expired one that has been soaked in $1.0 \times 10^{-5} \text{M}$ solution of Mg(II) for 35 days. The spectra were scanned for Mg 1s, O 1s, N 1s, C 1s, Cl 2p and Mg 2p electrons at a take-off angle of 35 degree. Figure 2 shows the N 1s band while TABLE 2 comprises the quantification data of all the bands.

The results indicated that in case of the expired membrane, the normalized peak area and atomic % of Mg 1s, Mg 2p and N 1s, which may be considered as tracers for the chlorophyll moiety, were much less than the corresponding values for the fresh membrane. This proves that the limitation in the life time of the electrode may be attributed to leaching of the ionophore from the gel layer to the bathing solution. The O 1s and C 1s peak areas and atomic % decreased also as in case of Mg 1s, Mg 2p and N 1s but to a greater extent. This revealed that not only the ionophore that leaches from

the membrane surface but also the plasticizer, resulting in a greater loss in O and C contents.

It is also noteworthy from figure 2 that the band for the N 1s photoelectrons, in case of the expired membrane, is characterized with significant background count while in case of the fresh one, the band is rather soft. This is most probably attributed to the effect of the different electrostatic environments around the atoms resulting from the hydration processes associated with the gel layer formation which do not exist in case of the fresh membrane. This is in accordance with previous results obtained for membranes containing ion-pair and ion-associate as exchangers^[17].

CONCLUSION

Naturally occurring chelates like chlorophyll may be employed as ion exchangers for the construction of ion-selective electrodes for metal cations. Chlorophyll was very successful as ionophore for Mg(II). The limitation of the life span of plastic membrane electrodes is attributed to leaching of the active ingredient and plasticizer to the test solution.

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