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Electrochemical Detection of Magnesium Ions Using PVC Membrane Trapped Chlorophyll A Molecules

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This paper presents a novel PVC membrane electrochemical biosensor for Mg^{2+} ions based on chlorophyll a as bioelectroactive membrane carrier. The sensor displays a Nernstian response for Mg^{2+} concentration range from 1×10^{-5} M to 1×10^{-1} M with a slope of 30.41 mV. The response time and selectivity for Mg^{2+} in comparison to some other cations have also been studied.

Keywords Biosensor; Magnesium Ion; Chlorophyll; PVC Membrane Electrode

INTRODUCTION

Intracellular Mg^{2+} is essential for mediating enzymatic reactions, DNA synthesis, hormonal secretion and muscular contraction. The determination and monitoring of Mg^{2+} concentration is essential for life science research and accurate diagnostic in health care.

Synthetic neutral carriers have been used as ion-sensing component in Mg^{2+} electrode[1-3]. More recently, fluorescent dyes have been used for Mg^{2+} concentration measurement. However, all these methods require either ion carriers or dyes that were prepared from

tedious synthetic and purification steps.

In this study, we report the use of chlorophyll a molecules as natural membrane carrier in the construction of a novel poly(vinyl chloride) (PVC) membrane biosensor for Mg^{2+} determination.

EXPERIMENTAL

All salts employed were of analytical grade. The standard stock solutions (0.1M) of magnesium chloride were prepared in double-distilled water; working solutions were obtained by dilution of the stock solution with double-distilled water. The pH was adjusted by the addition of hydrochloric acid or sodium hydroxide solutions.

Chlorophyll a was extracted from spinach (*Spinacia deracea* L.) leaves and purified by cellulose chromatography as described by Iriyama et al[4]. High molecular weight PVC and o-nitrophenyl octyl ether (o-NPOE) were obtained from Fluka. Freshly distilled tetrahydrofurane (THF) was used as a solvent for the membrane components.

The general procedure to prepare the PVC membrane was to dissolve 20 mg chlorophyll a in 2.5 ml THF, then add 200 mg *o*-NPOE as plasticizer and 2.5 ml 5% PVC solution in THF, all the compounds were mixed thoroughly. The resulting mixture was transferred into a glass dish with an inner diameter of 30 mm. After transfer, the solvent was evaporated naturally overnight. An elastic transparent membrane *ca.* 0.3 mm thick was thus obtained.

A disc of the membrane was cut out and mounted to a PVC tube (10 mm i.d.). The tube was then filled with internal filling solution

(1.0×10^{-3} M $MgCl_2$, AgCl saturated). The prepared sensor was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M solution of $MgCl_2$. Ag/AgCl coated wire was used as an internal reference electrode.

All emf measurements were carried out with the following cell assembly.

Hg; Hg_2Cl_2, KCl (0.1 M) || Test solution | PVC membrane | internal solution (1.0×10^{-3} M $MgCl_2$, AgCl saturated) | AgCl; Ag.

A PXJ-1B ion analyzer pH/mV meter was used for the direct potential measurements at 25.0±0.1 °C. The emf observations were made relative to a calomel electrode as external reference electrode. The performance of the electrodes was examined by measuring the emf of primary ion solutions in the concentration range of 10^{-7}-10^{-1} M.

Selectivity coefficients were determined for several ions using the fixed interference method by increasing the activity of primary ion in the solution. The activities of ions in aqueous solutions were calculated according to the Debye-Huckel approximation.

RESULTS AND DISCUSSION

Potentiometric chemical sensors with high ionic selectivity are especially suitable for the fast determination and monitoring of the concentration of Mg^{2+} in aqueous media, giving results with acceptable accuracy and precision, without necessity of complicated sample preparation.

Besides the synthetic Mg^{2+} carriers, the specific binding of Mg^{2+} to porphyrin involved in chlorophylls opens a new class of bioactive magnesium ion carrier. Although an occasional molecule of copper

chlorophyll or some other heavy metal chlorophyll might be present *in vivo*, they can be inserted into and removed from the porphyrin quite easily. Chlorophyll a is the most abundant form of chlorophyll within photosynthetic organisms, and it was used in this experiment.

The emf response of the PVC membrane magnesium ion biosensor can be described by the following Nernst equation:

$$E_m = E^0 + \frac{RT}{nF}\ln(a_i + K_{Mg}^{pot} a_j) \qquad (1)$$

where E_m is the sensor response, E^0 is the reference potential, a_i and a_j are activities of the primary ion and that of the interference in sample solution respectively, and K_{Mg}^{pot} is the selectivity coefficient. Figure 1 shows a representative emf response function of the Mg^{2+} biosensor based on chlorophyll a as membrane carrier. From this figure we can see that the slope of the sensor response is 30.41 mV.decade^{-1}, with a detection limit of 3.2×10^{-6} M. This result is in good agreement with the theoretical value calculated from equation (1) where a predicted slope is 29.58 mV.

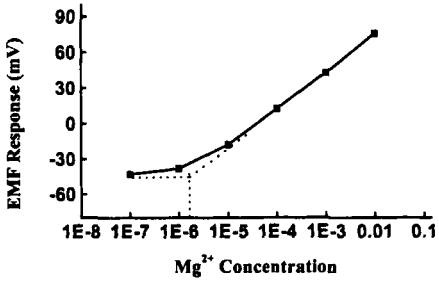

FIGURE 1. The emf response of the magnesium ion biosensor.

The response time of this biosensor at various Mg^{2+} concentrations is from 10 s to 2 minutes, and further optimization of the

membrane composition is needed to improve the response time at low Mg^{2+} concentrations.

The selectivity behavior is obviously one of the most important characteristics of an ion sensor, determining whether a reliable measurement in the sample is possible. Selectivity of the sensor was accessed through fixed solution method by using the equation:

$$K_{Mg}^{Pot} a_I^{i/n} = a_{Mg}\{\exp[(E_2 - E_1)F/RT]\} - a_{Mg} \quad (2)$$

where E_1 and E_2 are the sensor potentials for the solution of Mg^{2+} alone and for the solution containing interfering ions and Mg^{2+} ions, respectively. The resulting K_{Mg}^{Pot} values are illustrated in Figure 2.

The influence of of pH on the response of this biosensor to 1×10^{-2} M $MgCl_2$ solution over a pH range from 2 to 10 was studied. The results showed that the optimal working pH is from 6.0 to 8.0.

From recovery test, the average recovery is calculated to be 100.4%.

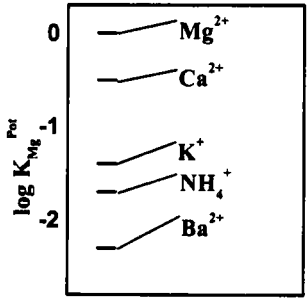

FIGURE 2. Potentiometric selectivity versus interfering ions.

CONCLUSIONS

The chlorophyll a appears to be an idea Mg^{2+} carrier for the fabrication of Mg^{2+} biosensor. However, in order to improve the performance of this biosensor, especially the high specific recognition ability, a deep understanding of the structure and function of *in vivo* Mg^{2+}-chlorophyll-photosynthetic protein complex is need.

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