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GELATINE MEMBRANE ELECTRODE SENSITIVE TO ALKALINE EARTH METAL IONS IN DIMETHYL SULFOXIDE

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A gelatine membrane electrode coated on a copper disk was found to respond in DMSO in a Nernstian way to the activities of magnesium and calcium ions and in a near-Nernstian way to that of barium ion. The approximate selectivity coefficients for the magnesium and barium ions vs. the calcium ion were 0.4 and 0.7, respectively. The electrode also responded linearly to $pa_{Zn}2+$ and $pa_{Cu}2+$, but with slopes larger than the Nernstian one.

Ion-selective electrodes nowadays available have been prepared for use in aqueous solutions, and many of them are difficult to apply in non-aqueous solutions. Besides the problem of the proper response of the electrodes, the materials constructing the electrodes should not be damaged in the solvents used. From this point of view, glass electrodes and some solid membrane electrodes are promising. Actually these electrodes have recently been used successfully in non-aqueous and mixed solvents for various physicochemical and analytical studies.[1-4] When we consider the usefulness of these electrodes, the efforts to develop other ion-selective electrodes applicable in non-aqueous solutions seems to be worthwhile.

Recently we have studied the behavior of some organic polymer membrane electrodes in non-aqueous solvents, and found that a gelatin membrane electrode coated on a copper disk was durable in dimethyl sulfoxide(DMSO) and could respond in a Nernstian way to the activities of the magnesium and the calcium ions and in a near-Nernstian way to that of the barium ion in DMSO. Some preliminary results are going to be described in this report.

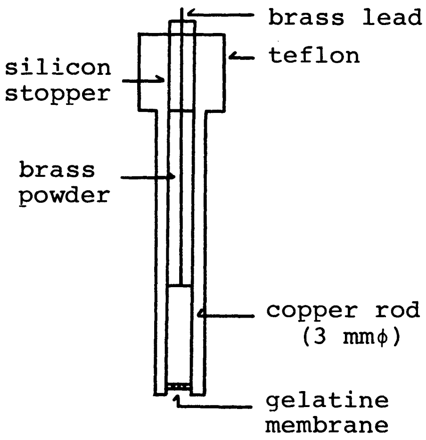

Fig.1. Schematic diagram of the gelatine membrane electrode

The gelatine membrane electrode as shown in Fig.1 was prepared by putting 10 µl aqueous gelatine solution (50 mg gelatine/ml) at 70 °C onto the surface of the copper disk electrode and by standing it for one day at room temperature to form the gelatine membrane. The response of the electrode was tested by measuring emfs of the following cell,

$$\mathrm{Ag}\,|\,0.005\mathrm{M}\ \mathrm{AgNO_3} + 0.01\mathrm{M}\ \mathrm{Et_4NClO_4(DMSO)}\,\|\,0.05\mathrm{M}\ \mathrm{Et_4NClO_4(DMSO)}\,\|$$

$$c\ \mathrm{M(ClO_4)_x} + 0.01\mathrm{M}\ \mathrm{Et_4NClO_4(DMSO)}\,|\,\text{gelatine membrane electrode} \ \ldots\ \text{Cell I}$$

where $M(ClO_4)_x$ was magnesium, calcium, barium, zinc(II), copper(II), or sodium perchlorate. To obtain a calibration curve, the concentration c of $M(ClO_4)_x$ was increased, unless otherwise stated, stepwise by the standard addition method. Before obtaining each calibration curve, the gelatine electrode was immersed in a DMSO-0.01M Et_4NClO_4 solution in the sample compartment of Cell I and stood until it showed a stable potential against the Ag/Ag^+ reference electrode. The gelatine and the reference electrodes were freshly prepared every day. All measurements were carried out at 25 °C.

Calcium perchlorate, prepared from aqueous calcium hydroxide and perchloric acid, was recrystallized from DMSO and dried at 100 °C under vacuum. It was found to be $Ca(ClO_4)_2\cdot 6DMSO$ by the EDTA titration. Zinc and copper perchlorates, obtained from Nakarai Chemicals Co. Ltd., were recrystallized from DMSO and dried at 80 °C under vacuum. Their compositions were confirmed to be $Zn(ClO_4)_2\cdot 4DMSO$ and $Cu(ClO_4)_2\cdot 4DMSO$, respectively, by EDTA titrations. Unhydrated magnesium, barium and sodium perchlorates were of analytical reagent grade and were used after being dried at appropriate temperatures. Gelatine powder was a product of Merck(Art. 4078-9004865). Dimethyl sulfoxide of reagent grade was distilled twice under vacuum after being dried over molecular seives 3A. Other apparatus and reagents were the same as those used in the previous report.[5)]

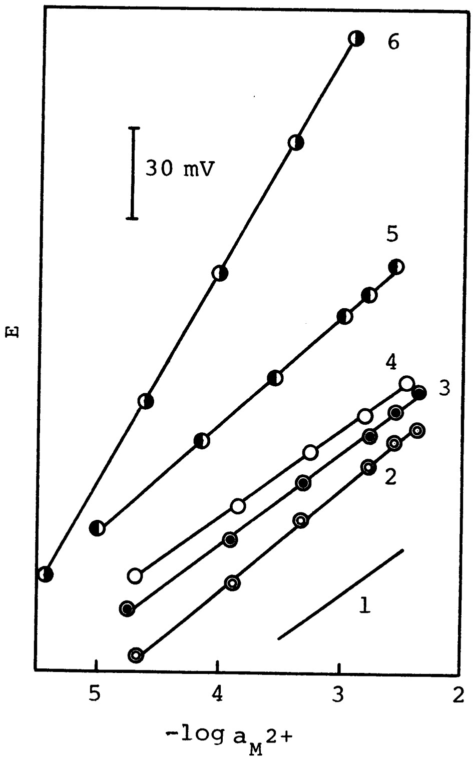

Fig.2. Calibration curves

Line 1, theoretical slope (29.6 mV/$pa_{M^{2+}}$); 2, Ba^{2+}; 3, Mg^{2+}; 4, Ca^{2+} ; 5, Zn^{2+}; 6, Cu^{2+}.

The response of the gelatine membrane electrode to the magnesium, calcium, barium, zinc(II), copper(II), and sodium ions in DMSO was investigated. The calibration curves were obtained by the standard addition method and some of the results are shown in Fig.2. In Table 1 the results of the response of the electrode to these divalent cations in DMSO are summerized. The activity of the metal ion, $a_{M^{x+}}$, was calculated by using the equation $a_{M^{x+}} = cy$, where c was the concentration of M^{x+} in mol dm^{-3} , and y the activity coefficient of M^{x+} obtained from $\log y = -Ax^2 I_c^{1/2} [1 + BaI_c^{1/2}]^{-1}$ ($A = 1.11$ mol$^{-1/2}$ dm$^{3/2}$, $B = 4.26 \times 10^8$ mol$^{-1/2}$ dm$^{1/2}$, $a = 5 \times 10^{-9}$ dm, and I_c = ionic strength). The results in Table 1 have not been corrected for the liquid junction potential between the sample solution and the salt bridge of Cell I, because the equivalent conductivity data necessary for their calculation are not available.

Table 1. The response of the gelatine membrane electrode to several divalent cations in DMSO at 25 °C

Ions	Slope mV/$pa_{M}2+$ (mV/$pc_{M}2+$)	Range of the linear response $pa_{M}2+$ ($pc_{M}2+$)	Approximate selectivity coefficient ($K_{Ca^{2+},M^{2+}}$)
Mg^{2+}	29.5 ± 0.6 (25.8 ± 0.6)	4.8 - 2.4 (4.3 - 1.6)	0.4
Ca^{2+}	29.8 ± 0.8 (26.3 ± 0.7	4.7 - 2.5 (4.3 - 1.8)	(1)
Ba^{2+}	33.0, 33.5 (28.1, 28.6)	4.7 - 2.4 (4.3 - 1.6)	0.7
Zn^{2+}	35.4, 37.4 (31.8, 32.8)	5.0 - 2.7 (4.5 - 1.8)	-
Cu^{2+}	77.2 ± 7.3 (72.3 ± 5.6)	5.4 - 2.9 (5.1 - 2.4)	-

From Table 1, it is apparent that the membrane electrode responded in a Nernstian way to the activities of the magnesium and the calcium ions and in a near -Nernstian way to that of the barium ion between 5×10^{-5}M and about 0.02M. For the calcium ion the electrode was also confirmed to respond in a Nernstian way even when its concentration was decreased stepwise from about 0.02 to 5×10^{-5}M by exchanging the sample solution of Cell I. The rates of the electrode response to these ions were fairly rapid and, at each activity of these ions, the electrode reached the corresponding equilibrium potential within 30 seconds.

The approximate selectivity coefficients for the magnesium and the barium ions vs. the calcium ion, $K_{Ca^{2+},M^{2+}}$, obtained by mixed solution method, are also shown in Table 1. The results show that this electrode had an approximately similar sensitivity to all these ions.

The gelatine membrane electrode also responded linearly to $pa_{Zn}2+$ and $pa_{Cu}2+$. However, the slope for the zinc(II) ion was a little larger than the Nernstian slope, and that for the copper(II) ion was super-Nernstian. The rates of the potential response for these ions were much slower than the cases of alkaline earth metal ions, and they decreased with the increase of the concentration of the metal ions. These deviations of the electrode behavior from the ideal one may be caused by the complex formation of these metal ions with gelatine.[6,7] The response of the gelatine membrane electrode to the sodium ion was also examined, but it did not respond linearly to pa_{Na^+}.

As shown above, the response of the gelatine membrane electrode to alkaline earth metal ions in DMSO was Nernstian or near-Nernstian. Though the selectivity of the electrode is not sufficient, it is applicable, at the present stage, to know the activity and to investigate the complexing of a single alkaline earth metal ion in DMSO.

Further investigations are now in progress in this laboratory to elucidate the mechanism of its response, to improve its selectivity, and to apply for various practical purposes.

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