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VITAMIN-SENSITIVE ELECTRODES WITH A LIQUID MEMBRANE

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Ion-selective electrode membranes responsive to vitamin B_1 and vitamin B_6 were prepared by using ion-association extraction systems. The liquid membrane electrodes exhibit appropriate Nernstian responses to vitamin B_1 and vitamin B_6 ions down to 10^{-5} M. High selectivities for vitamin B_1 and vitamin B_6 over Na^+, NH_4^+, and K^+ were observed.

Various kinds of ion-selective electrodes have been developed as a noticeable analytical sensor in recent years. The liquid membrane electrodes may be characterized by possibility of the preparation of organic ion-selective electrode. Coetzee and Freiser reported that many organic ion-association extraction systems are utilizable as the membrane materials of the ion-selective electrodes.[1] This letter describes that vitamin B_1 and vitamin B_6 are easily extracted into organic solvents such as 1,2-dichloroethane and nitrobenzene with tetraphenylborate or dipicrylamine anion from acidic aqueous media (pH 3-5) and these organic solutions can be used as the corresponding vitamin-sensitive membranes.

Nitrobenzene and 1,2-dichloroethane were good membrane solvents from the standpoint of the extractability and electrical conductivity, whereas chloroform and monochlorobenzene were not suitable.

Preparation of the liquid membrane and the performance of the electrode membrane.

Ten ml of 1×10^{-3} M vitamin B_1 hydrochloride solution was mixed with 20 ml of equimolar sodium tetraphenylborate solution and then with 50 ml of distilled water. The resulting aqueous solution was shaken with 100 ml of 1,2-dichloroethane for 60 min. The organic phase, which was separated from the aqueous phase, was shaken again with 100 ml of 1×10^{-3} M vitamin B_1 solution for purification. After the phase separation was completed, the organic solution was filtered through a dried filter paper and it was used as the vitamin B_1-sensitive liquid membrane. The vitamin B_6-sensitive liquid membrane was also prepared in a similar manner. The extractants (exchange site of liquid membrane) and organic solvents were shown in Table 1. The concentration of the membrane solute was 1×10^{-4} M. The electromotive force (membrane potential) of the following cell was measured with a Takeda-Riken electrometer TR-8651 in order to evaluate the membrane performance.

$$\oplus \text{ SCE / Reference solution / } \underbrace{\text{Organic liquid membrane}}_{\text{(Electrode)}} \text{ / Sample solution / SCE } \ominus$$

The cell assembly is the same as that described elsewhere.[2]

Acidic aqueous solution of vitamin B_6 is stable, but the aqueous solution of

vitamin B_1 is comparatively stable only in the range of pH 2-4.[3] The vitamin B_1 solution, therefore, was prepared immediately before the measurement of membrane potential. Figure 1 shows the electrode responses to vitamin B_1 and vitamin B_6 ions. The electrodes exhibit typical responses to bivalent (B_1) and univalent (B_6) cations. The potential slopes of the electrodes are nearly Nernstian to vitamin B_1 and vitamin B_6 ions throughout the concentration of 10^{-2} to 10^{-5} M. The deviation from the Nernstian behavior at lower concentrationof vitamin ion is probably due to the elution of the membrane solute to adjacent aqueous solution, and the deviation at higher concentration is due to taking no account of activity coefficients. The selectivity coefficients were determined by using the separate solution method.[4] The outline of the electrode performance including selectivity was given in Table 1. It can be seen that the electrodes have the high selectivities for vitamin ions over Na^+, NH_4^+, and K^+ ions.

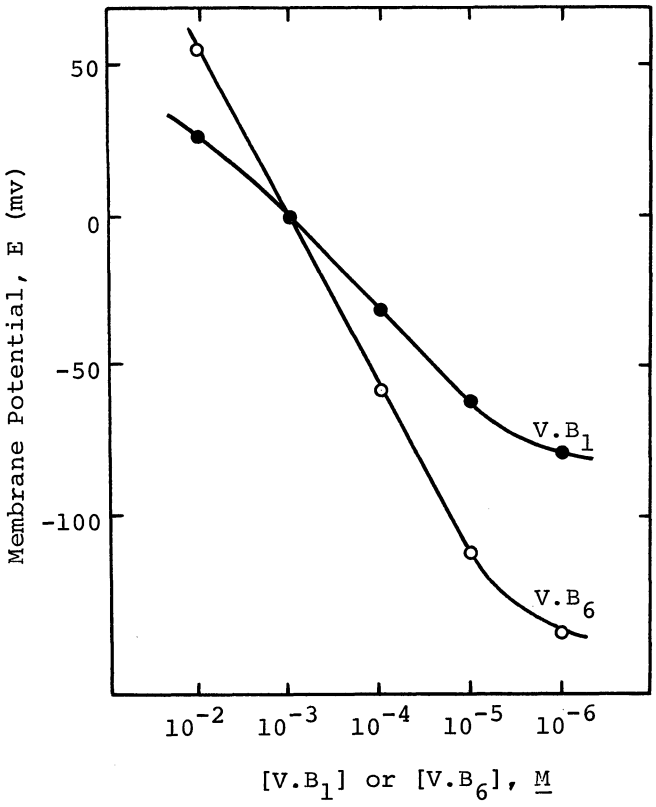

Figure 1. Responses of the vitamin-sensitive electrodes (27°C)

Table 1. Performance of the vitamin-sensitive electrodes

electrode	solvent	exchange site	slope,-mv/logC*	useful range	selectivity coefficients
Vitamin B_1	1,2-dichloroethane	tetraphenylborate	-30	10^{-2}-10^{-5} M	NH_4^+ 1×10^{-4}, Na^+ 10^{-4}, K^+ 10^{-4}, V.B_6 70
Vitamin B_6	nitrobenzene	dipicrylamine	-57	10^{-2}-10^{-5} M	NH_4^+ 8×10^{-3}, Na^+ 6×10^{-4}, K^+ 2.5×10^{-2}, V.B_1 1×10^{-1}

*) C denotes the molar concentration of vitamin ion.

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References.

1) C. J. Coetzee and H. Freiser, Anal. Chem., 40, 2073 (1968), 41, 1128 (1969).
2) N. Ishibashi and H. Kohara, Anal. Letters, 4, 785 (1971).
3) "Japanese Pharmacopoeia" VII-I, part I, Hirokawa, p. 295.
4) G. J. Moody and J. D. R. Thomas, " Selective Ion Sensitive Electrodes" Merrow Pub. Co. Ltd., Watford, Herfordshire, Eng. (1971), p.12.

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