Letters to the Editor

Vitamin B₁-Sensitive Poly(vinyl chloride) Membrane Electrode Based on Hydrophobic Tetraphenylborate Cation Exchangers

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There have been many papers on liquid membrane and solvent polymeric membrane electrodes sensitive to drug substances.^{1,2} Most of these electrodes are based on liquid ion-exchangers. One of the disadvantages of these types of electrodes is their short lifetime. This is due to dissolution of the ion exchanger in the membrane into a sample solution, which leads to a decrease in sensitivity of the electrode.^{3,4} To maintain the sensitivity of the electrode by using more hydrophobic ion exchangers was thought to be one way to solve problem.

Recently, two (T.S. and H.K.) of the authors prepared tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB), which shows high acid-resistivity and has high hydrophobicity.⁵ TFPB is expected to be an excellent cation exchanger for many kinds of liquid cation exchange membrane electrodes having high sensitivity. In this paper, we briefly report on a highly sensitive new vitamin B₁ electrode, which uses TFPB and its analogue with more hydrophobic substituent groups.

Experimental

The cation exchangers used are shown in Fig. 1. Borate 1 was prepared as a sodium salt. Details of the preparation will be described later.⁶ Borates 2–5 were obtained from Dojin Laboratory as sodium or potassium salts. A sodium salt of dipicrylamine was obtained from Kishida Kagaku Co. The poly(vinyl chloride) (PVC) membrane plasticized with *o*-nitrophenyl octyl ether (NPOE) was prepared by the following procedure. NPOE (1.0 g), PVC (0.4 g) and a cation exchanger (4–18 mg) were dissolved by 10 ml of tetrahydrofuran (THF). The THF solution was poured onto a flat-bottomed glass dish (i.d. 6.8 cm) and THF was allowed to evaporate by 48 h standing at room temperature to obtain the plasticized PVC membrane. The concentration of the cation exchanger in the plasticized PVC membrane thus obtained is approximately 10⁻² mol/l-NPOE. A disk (diameter 7 mm) was cut out from the obtained membrane and was fitted to an ion selective electrode body (Denki Kagaku Keiki Co.). After filling an inner solution (a mixed solution of 1×10⁻² M NaCl and 1×10⁻² M vitamin B₁) and inserting an inner electrode (Ag₂S–AgCl electrode) into the electrode body, the electrode was immersed into the 0.1 M vitamin B₁ solution for 15–24 h for conditioning of the electrode membrane. The performance of the electrode was examined by measuring the emf of the following electrochemical cell:

Fig. 1 Cation exchangers used in this work.

Results and Discussion

The ionized form of vitamin B₁ and its chemical

Fig. 2 Calibration curves of the electrodes based on several cation exchangers for vitamin B₁.

stability are dependent on the pH of the sample solution. Vitamin B₁ exists as a divalent cation and is stable in the solution around pH 4. Indeed, the electrode potential was almost constant for the solution of pH 2–4.5, but varied with pH in solutions higher than pH 5. Therefore, the performance of the electrode was examined for the sample solution maintained at pH 4 by adding 0.1 M acetate buffer solution.

Figure 2 shows the calibration curves of the vitamin B₁-sensitive electrodes, based on several cation exchangers. The electrode based on borate 1 shows the Nernstian response (the slope of the potential was 30 mV/decade) to the vitamin B₁ from 10⁻² M to 10^{-7.5} M. The electrode based on borate 1 has the highest sensitivity so far examined in the present work and is more excellent

in sensitivity than the 1,2-dichloroethane membrane electrode based on borate 5, which was reported previously.⁷ The sensitivity decreases in the order of the electrode based on the borates 1>2 (TFPB)=3>4>5, which is in parallel with that of hydrophobicities of the borates.

The potentials of the electrodes based on the borates 1 and 2 are highly reproducible. The variation of the potential in repeated measurements was less than 2 mV for the vitamin B₁ solutions higher than 10⁻⁵ M. No potential drift or variation of slope of the electrode potential have been observed during at least 70 d of continuous use, even in flow system. The electrodes have short response times 10 s–1 min. The selectivity of the electrode to vitamin B₁ over Na⁺, K⁺ and vitamin B₆ is almost the same as that reported previously.⁷ The presence of glutamic acid, glucose or lactic acid did not interfere with determination of 10⁻⁴ M vitamin B₁, which indicates that the electrodes may be useful in food or pharmaceutical analyses.

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