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A Gel-state Liquid-membrane Iodide-ion Electrode

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Synopsis. A new liquid-membrane iodide-ion electrode has been developed. The liquid membrane of the electrode consists of poly vinyl chloride gel containing a nitrobenzene solution of tridodecylethylammonium iodide as an ion exchanger, a lead wire is inserted directly into the gel. The properties of the electrode, such as the response time, the effect of the temperature, the reproducibility of the preparation, and the selectivity, have been determined.

Recently, a number of studies of the simplification of the construction of liquid-membrane ion electrodes have been carried out. James *et al.*[1] developed coated-wire ion-selective electrodes with a fine platinum wire covered with poly vinyl chloride film containing an ion-association complex. Ruzicka and Rald[2] developed a simple liquid-state ion electrode, named selectrode, consisting of a graphite rod impregnated with the liquid-membrane, it was put in a Teflon tube. A stainless steel wire screwed into the graphite rod served as a lead to an electronic voltmeter. We prepared a simple liquid-membrane ion electrode consisting of a gel-state liquid-membrane and a lead wire inserted directly into the gel phase. Further, the effects of various conditions on the properties of the gel-state liquid-membrane were examined.

Experimental

A Hitachi-Horiba Model F-7 SS pH meter was used for the potential measurements. The tridodecylethylammonium bromide (TDEA) was prepared according to the method of a previous paper.[3]

The electrode body consisted of a glass tube, 8—10 mm in diameter and fitted with rubber and cork stoppers, as is shown in Fig. 1. A stainless steel wire 2 mm in diameter inserted into the gel membrane served as a lead to an electronic voltmeter. The ion-association complex solution was prepared by repeatedly shaking a nitrobenzene solution of 1×10^{-4} M TDEA with an aqueous solution of 1×10^{-3} M potassium iodide. The gel-state liquid-membrane was prepared by the following procedure. A 5 ml portion of the ion-associate solution was mixed with 0.9 g of poly vinyl chloride (PVC) in a test tube. The mixture was heated to 100 °C in an oil bath and stirred until the PVC has been completely dissolved. This solution was then poured into the B part of the electrode body and gelatinized by cooling to room temperature. The gel-state liquid-membrane electrode was preserved over nitrobenzene in a bottle fitted with a cork stopper. All the potentials were measured against a saturated calomel electrode as the reference electrode at 25.0±0.1 °C. The gel-state liquid-membrane electrode was dipped in the ion-associate solution for 1 s before use.

Results and Discussion

The variation in the potential of the gel-state liquid-membrane electrode with the concentration of the iodide ions is shown in Fig. 2. The calibration curve is linear down to 1×10^{-5} M iodide. The response of this gel-state liquid-membrane electrode was fairly fast and attained an equilibrium potential after a 2-min dipping of the electrode into the test iodide solution beyond 1×10^{-5} M. Below 1×10^{-6} M iodide, however, the equilibrium potential was attained only after 10 min. The effects of the concentration of the ion associate in nitrobenzene on the potential were examined. Four electrodes with varying concentrations of TDEA in nitrobenzene were made by the above-mentioned procedure. The variation in the potential with the concentration of iodide for each electrode is shown in Fig. 3. A better linearity of the potential variation and a higher sensitivity were obtained for the electrode with the membrane of the concentration of the ion associate of 1×10^{-4} or 7×10^{-5} M.

The surface of the gel-state liquid-membrane gradually became softer with the rise in the temperature and was

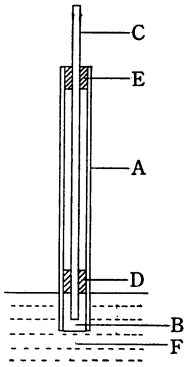

Fig. 1. Construction of the gel-state liquid-membrane electrode.
(A) glass tube, (B) gel state liquid membrane, (C) lead wire, (D) cork stopper, (E) rubber stopper, (F) test solution.

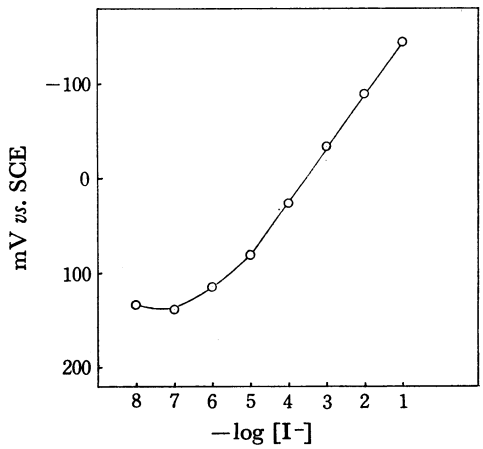

Fig. 2. Calibration curve.
Ion associate: 1×10^{-4} M

Table 1. Summary of the properties of iodide-responsive electrodes

Electrode	Ion exchanger	Slope (mV/log a)	Concn range of linear response	Selectivity ratios (NO^-_3)
Gel state liquid membrane electrode	Tridodecylethylammonium salt	56.0	10^{-1}—10^{-5}	0.058
Coarted wire[1] electrode	Tricaprylmethylammonium salt	60.0	10^{-1}—10^{-4}	0.11
Liquid membrane[5] electrode	Tricaprylmethylammonium salt	59.0	10^{-1}—10^{-3}	0.19

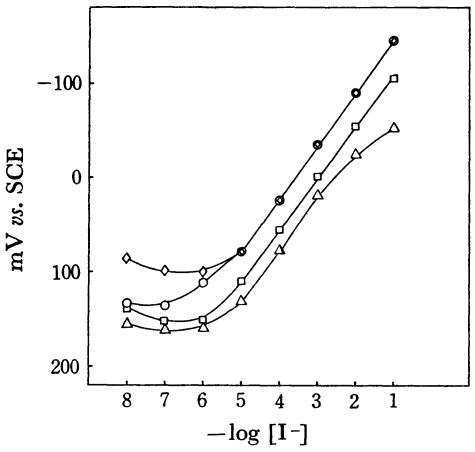

Fig. 3. Effect of concentration of the ion associate in nitrobenzene on potentials
Ion associate: △; 1×10^{-5} M, □; 7×10^{-5} M, ○; 1×10^{-4} M, ◇; 1×10^{-3} M.

deformed a little beyond 40 °C. The variation in the potential was small below 30 °C, but the potential dropped suddenly above 35 °C. Therefore, the temperature of the test solution must be kept constant below 30 °C. The pH variation in the test solution showed that the potential did not change over the pH range of 3—9. The reproducibility of the preparation of the electrode was also examined. Five pieces of electrodes were made by the above-mentioned procedure. The potentials of the electrodes for the same concentration of the iodide solution were fairly different, but the slopes of the potential variation for all the electrodes were nearly the same in the concentration range of iodide of 1×10^{-5}—1×10^{-1} M.

The gel-state liquid-membrane deteriorated on exposure to air because of the evaporation of the solvent. Therefore, the electrode should be stored over nitrobenzene in a bottle fitted with a cork stopper. If the electrode was dipped in a 1×10^{-4} M ion-associate solution before employment, the electrode could be used for two months. The influence of foreign anions on the determination of iodide was examined by adding various salts to the 1×10^{-4} M iodide solution. The selectivity ratios, as calculated by the same procedure as that of Rechnitz,[4] were 56 for perchlorate, 2.8 for thiocyanate, 0.058 for nitrate, 0.013 for cyanide, and 0.0047 for bromide.

The properties of the gel-state liquid-membrane electrode are compared with those of other, similar iodide electrodes in Table 1.

References

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