Alkyd Resin Paint as a New Membrane Material of Ion-selective Electrode

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A new membrane material, alkyd resin paint, was used for a silver iodide-based ion-selective electrode. The electrode was easily prepared in the laboratory by mixing silver iodide precipitate and alkyd resin paint. The electrode responded to both iodide and silver ions with the deviations from a Nernstian response due to adsorption and desorption of ions. Silver ions tended to adsorb more strongly on the electrode surface. The preparation and properties of the present electrode are described in view of an analytical utilization of the electrode.

Various membrane materials including silicone rubber, poly(vinyl chloride), and paraffin wax have been utilized for the precipitate-based ion-selective electrode.[1] We are interested in the development of a new electrode material which is easily prepared in a laboratory. The following conditions are required for the membrane materials of the precipitate-based ion-selective electrode:[2] (a) It is chemically inert and provides good adhesion for the sensor precipitates. (b) It is hydrophobic, tough, flexible, nonporous, and non-swelling in sample solution. Extensive swelling disrupts the active chain of the sensor precipitates.

In the present study, we chose alkyd resin paint as a membrane material, because it is most commonly utilized for outdoor painting, and it provides a chemically tough and weather-proof coating. In addition, it can well disperse the inorganic pigments in the paint medium.[3,4] This paper describes the use of the alkyd resin paint to a silver iodide-based ion-selective electrode. The electrode was prepared by the incorporation of silver iodide into the alkyd paint. This electrode responded well to both iodide and silver ions. The deviations from a Nernstian response, attributed to the adsorption and desorption of ions,[5] were observed at a lower concentration region. The characteristics of the electrode were discussed in view of an analytical utilization of the electrode.

Experimental

Reagents. Silver iodide was purchased from Rare Metallic Co., Ltd., and alkyd resin paint was a product of Nippon Oil and Fats Co., Ltd. (Glasstone No. 1000, Clear). Other chemicals used were all of analytical reagent grade. Water was distilled and deionized.

Preparation of Electrode. Figure 1 shows the silver iodide-based ion-selective electrode constructed in the present study. A copper plate (*ca.* 10 mm diameter, 0.5 mm thickness), which was connected to a shielded cable, was covered with a glass tube, and tightly attached using an epoxy resin adhesive. The exposed copper plate was polished with sandpaper, washed, and dried. Silver iodide was sieved through a 200-mesh screen after grinding in a mortar. Alkyd resin paint was diluted with toluene (20 w/w%) in order to decrease its viscosity. The silver iodide powder and the diluted paint were then blended on the copper plate, and the mixture was allowed to dry in air overnight. The mass ratio of the powder to the paint was not so critical, though the most favorable results were obtained with 15—20 mg of the powder and 20 ul of the diluted paint. The electrode

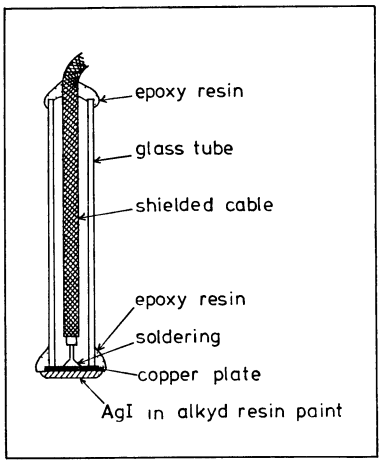

Fig. 1. Construction of electrode.

was used after being soaked for 2 h in 10^{-4} M† solution of potassium iodide.

Potential Measurements. The electrochemical cell assembly employed in this study is as follows: silver iodide-based ion-selective electrode/ test solution/ 1 M NH_4NO_3 (salt bridge)/ 0.01 M KCl/ Ag,AgCl. Usual glass containers were used for the stock of test solutions. The amount of test solution was 2 ml, and the ionic strength was maintained at 0.1 with KNO_3. An appropriate FET-operational amplifier (input resistance: $>10^{12}\,\Omega$) was used for the potential measurements. The measurements were carried out at room temperature. The solution was stirred with a magnetic stirrer. Between measurements, the electrode was rinsed several times with water and wiped.

Results and Discussion

Response Characteristics. Figure 2 shows the potential response to iodide ions of the present electrode. The calibration curves were measured from 10^{-7} M to 10^{-2} M of iodide ions, and three consecutive runs were performed. The lower detection limit of iodide ion was gradually interfered with repeated calibration measurements. Further deterioration of the detection limit, however, was not observed even when the electrode was continuously used. It was found that if the electrode was soaked in fresh 0.1 M KNO_3 solution for 10 min, the detection limit could easily be improved to the level in the original calibration. This means that some iodide ions in the electrolyte may weakly be adsorbed on the electrode surface, and such ions can not be eliminated by a conventional washing of

† 1 M=1 mol dm^{-3}.

the electrode.

To clarify the influence of the adsorption of ions on the electrode, we measured the potential response after the pretreatment with various concentrations of iodide ion. The electrode was immersed in a solution (2 ml) containing iodide ion for 3 min, rinsed with water, wiped, and then soaked in 10^{-7} M KI—0.1 M KNO_3 solution; the addition of 10^{-7} M KI in the solution afforded the reproducibility and the rapid response of the electrode potential. The potential-time responses of the electrode are shown in Fig. 3. It was found that the amount of the iodide ion released was nearly proportional to the pretreated concentration of iodide ion. Such a correlation seems to indicate that the adsorption and desorption occur at the electrode surface. The Freundlich adsorption isotherm is applicable to the adsorption from solution:

$$x = kC_{eq}^{1/n},$$

where x is the specific amount adsorbed, C_{eq} is the concentration at equilibrium, and k and $1/n$ are constants characterizing the substance adsorbed and adsorbing materials.[6] It is reasonable to postulate that C_{eq} and x can refer to the concentration of iodide ion pretreated and the amount released in 10^{-7} M KI solution, respectively. The log-log plots of x *vs.* C_{eq} gave the values of $k=2\times10^{-4}$ and $1/n=0.6$.

The above discussions should hold when the adsorbed iodide ions are completely desorbed by dipping the electrode into the solution. To see more directly the effect of the adsorption of iodide ion, we measured the potential response to silver ion after the pretreatment with iodide ion. A large negative deviation of the potential response to silver ion was observed immediately after the pretreatment of the electrode with iodide ions (Fig. 4(a)). A normal Nernstian response could be observed after the adsorbed iodide ion reacted completely with silver ion. However, when the electrode was immersed in fresh 0.1 M KNO_3 solution for 10 min prior to the measurement, such deviation was diminished (Fig. 4(b)). This observation was consistent with the result that the adsorbed iodide ion was easily desorbed by soaking the electrode into the solution, as already mentioned above.

In contrast, the response to iodide ion after the pretreatment with silver ion showed a large positive deviation even after the electrode was immersed in fresh 0.1 M KNO_3 (Fig. 5(b)). This seems to indicate that silver ions tend to adsorb more strongly on the electrode surface. It has been reported that metal ions adsorbed on the electrode can not be removed by dipping into water.[7] Effective removal has been accomplished only by physical rubbing with a cleanser.

It is now well known that the adsorption and desorption taking place at an electrode surface cause the deviations from a Nernstian response.[5] Adsorption and desorption phenomena interfere with the lower limit of detection; other sources of the deterioration

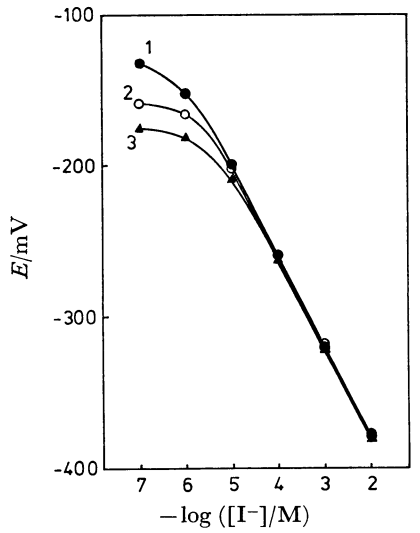

Fig. 2. Potential response to iodide ion. The calibration plots were measured in the order indicated. Three consecutive runs were performed.

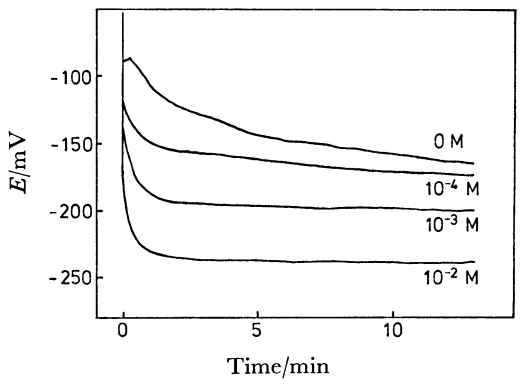

Fig. 3. Time course of the desorption of iodide ions after immersing the electrode in various concentrations of iodide ions for 3 min. The concentrations of the pretreatment are indicated in the figure. The electrode was soaked in a solution containing 10^{-7} M KI—0.1 M KNO_3.

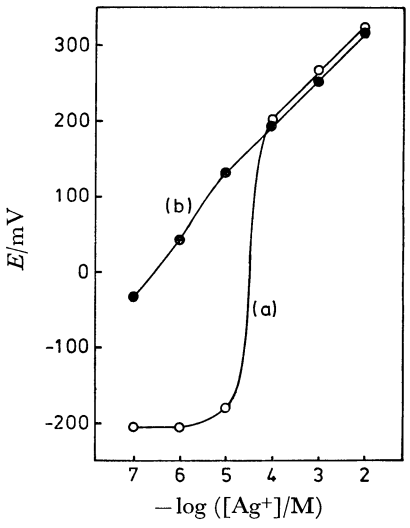

Fig. 4. Potential response to silver ion after the pretreatment of the electrode with 10^{-2} M iodide ion for 3 min. (a) Immediately after the pretreatment and conventional washing of the electrode. (b) After soaking in fresh 0.1 M KNO_3 solution for 10 min.

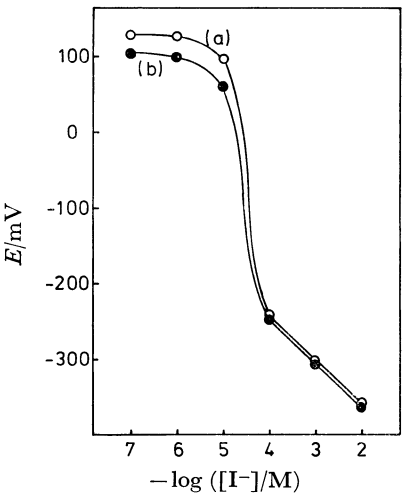

Fig. 5. Potential response to iodide ion after the pretreatment of the electrode with 10^{-2} M silver ion for 3 min. (a) Immediately after the pretreatment and conventional washing of the electrode. (b) After soaking in fresh 0.1 M KNO_3 solution for 10 min.

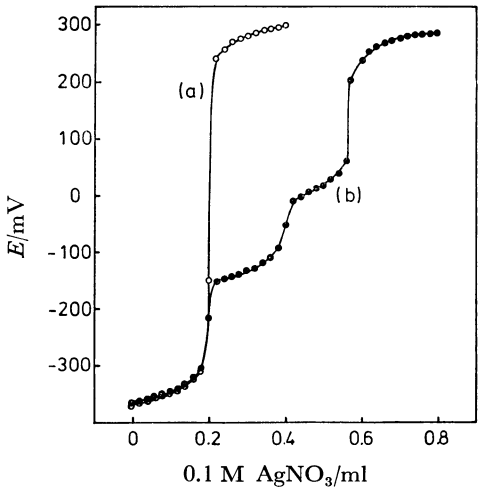

Fig. 6. Potentiometric titrations of iodide ion (a), and of a mixture of iodide, bromide, and chloride ions (b) at 0.01 M concentration in the presence of 0.1 M KNO_3.

(such as air oxidation of iodide ions) are also known.[8] It is quite natural to think that interference due to adsorption becomes more significant when the large surface area of the electrode and the small volume of the test solution are used. As for the iodide detection, if the present experiments were performed at iodide concentrations below 10^{-4} M (with 2 ml of test solution), it is unnecessary to consider the effects of adsorption and desorption because the interference at this concentration range is beyond the detection limit. Only when the measurement was transfered from higher (above 10^{-4} M) to lower concentrations, the cleaning of the electrode by soaking in a fresh solution without iodide ions was required.

Application to Potentiometric Titrations. Aside from the characteristics of the electrode, we tried an analytical utilization of the present electrode. Although an extensive application of the ion-selective electrode has been reported, the potentiometric titrations of iodide ion and of a mixture of iodide, bromide, and chloride ions were performed with the present electrode. A typical result is shown in Fig. 6. The well-defined S-shape of the titration curve and the large potential change at the end-point permitted accurate results, as was reported with silicone rubber membrane.[9] Potentiometric titrations could also be carried out in aqueous organic solvents (20% aqueous ethanol or acetone) and the halide content could be determined to be that obtained in aqueous solution.

Conclusion. The present paper describes the preparation and properties of the silver iodide-based ion-selective electrode with alkyd resin paint as a new membrane material. The experimental data presented here are almost compatible with the previous results; however, the most attractive point is ease of the preparation of the electrode in the laboratory. The electrode can be made without special treatments and techniques. Commercially available silver iodide and alkyd resin paint are blended on the metal surface. It is apparent that the present method will also be applied to the preparation of other electrodes by incorporating sensor precipitates into the alkyd resin paint.

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