A poly(vinyl chloride) membrane electrode that is highly sensitive and selective for zinc ions has been developed by using tetrabutyl thiuram disulfide neutral carrier. This electrode incorporated the ionophore along with o-nitrophenyloctyl ether as a plasticizing solvent mediator and potassium tetrakis(p-chlorophenyl)borate as anion excluder; it exhibited a linearity range of $10^{-1} - 10^{-6}$ M with a Nernstian slope of 28.0 mV per decade at 25±1°C. The membrane electrode showed a good response to zinc ions in the useful pH range of 3.5 to 6.5, where interferences arise only from a few transition metals such as Cu²⁺ and Pb²⁺.

Keywords Zinc-selective membrane electrode, zinc ion, neutral carrier, tetrabutyl thiuram disulfide

Experimental

Chemicals

Poly(vinyl chloride) (PVC) and o-nitrophenyloctyl ether (NPOE) were purchased from Fluka (Buchs, Switzerland). Potassium tetrakis(p-chlorophenyl)borate (KTCPB) used as anion excluder and the ionophore, TBTDS (Fig. 1) were obtained from Dojindo Laboratories (Kumamoto, Japan) and Tokyo Kasei Kogyo Co. (Tokyo, Japan), respectively. All other chemicals were the best laboratory reagents available and all solutions were prepared from analytical reagent grade salts using distilled de-ionized water.

Membrane composition and electrode fabrication

The method for preparing PVC immobilized ionophore membrane has been described previously. The polymeric sensor membrane was prepared by dissolving 20 mg of TBTDS, 200 mg of NPOE, 3 mg of KTCPB and 150 mg of PVC in tetrahydrofuran (THF) 5 ml. The THF solution was poured into a glass ring (35 mm diameter) on a glass plate and kept for 24 h at 30°C to form a sensing membrane. The electrode was made by mounting a disk (6 mm diameter, 0.2 mm thickness) of the membrane to the end of the electrode. The electrode fabrication is shown schematically in
ANALYTICAL SCIENCES  JUNE 1994, VOL. 10

Fig. 2. The electrode was soaked in 10^{-3} M Zn(NO_3)_2 solution for 24 h and then used by immersing in 10^{-3} M ZnCl_2 as the inner filling solution.

**Electrode system and emf measurement**

All emf measurements were performed with the following cell assembly: Ag-AgCl/10^{-3} M ZnCl_2/sensor membrane/sample solution/reference electrode. A Model HM 20E ion analyzer from TOA Electronics (Tokyo, Japan) was used for the measurement of the electrode potentials. The emf observations were made with reference to a double-junction type Ag-AgCl electrode, in a solution stirred by a magnetic stirrer, in the concentration range of 10^{-1} to 10^{-6} M of Zn^{2+} ion. The activity of the metal ion was based on the activity coefficient (\( \gamma \)) data calculated from the modified form of the Debye–Hückel equation:

\[
\log \gamma = -0.511 Z^2 \left[ \mu^{1/2}/(1 + 1.5 \mu^{1/2}) - 0.2 \mu \right]
\]

where \( \mu \) is the ionic strength of the medium and \( Z \) is the valence of the analyte ion. All the measurements were carried out at 25\( \pm \)1°C.

**Results and Discussion**

A typical calibration graph of the Zn^{2+}-selective membrane electrode is shown in Fig. 3. The membrane electrode showed a Nernstian slope of 28.0 mV per decade with a straight line between 10^{-1} and 10^{-6} M Zn(NO_3)_2. The detection limit for Zn^{2+} ion was 4.2 \times 10^{-6} M, which is lower than the value obtained for zinc electrode in previous reports.\(^{1-12}\) The effect of temperature on the electrode behavior was examined by constructing the calibration curves at 5 and 45°C. The electrode exhibited similar Nernstian behavior at these temperatures.

The response time of the electrode was determined by measuring the time required to achieve a steady-state potential, in 10^{-4} to 10^{-2} M and in 10^{-2} to 10^{-4} M Zn^{2+} solutions, by a rapid 100-fold increase and decrease in the zinc concentration. The electrode potential (mV) vs. time (s) profile obtained with a zinc-selective membrane electrode is shown in Fig. 4. At a 100-fold increase of the zinc ion concentration, the response time of the electrode for zinc ion was 2 s, while at a 100-fold decrease, it was 10 s. The response mechanism of the present electrode was considered fast.

The pH response of the electrode was examined in 10^{-3} M Zn(NO_3)_2 solution, where the pH was adjusted with nitric acid (0.1 M) and sodium hydroxide (0.1 M)
for acidic and alkaline ranges, respectively. The influence of pH on the electrode response is shown in Fig. 5. The membrane electrode provided a useful pH range of 3.5 – 6.5, applicable to ideal zinc electroplating solutions, where the pH values are usually in the range of 3.0 to 4.5. At pH values lower than 3.5, the potential increased with decreasing pH, indicating that the electrode responded positively to the hydrogen ion, while at pH values above 6.5, the electrode potential decreased due to the formation of zinc hydroxide in solution. The usability of the electrode may be demonstrated at higher pH range in ammoniacal medium. In a zinc solution of pH 10 adjusted with NH₄Cl-NH₃ buffer, the calibration curve for zinc ion response of the membrane electrode exhibited a Nernstian slope of 28 mV per decade, with a linearity range from 10⁻¹ to 10⁻⁶ M, similar to that in Fig. 3.

The selectivity coefficients (K_{Zn,B}^{pot}) (B designates an interfering metal ion) for the Zn²⁺ membrane electrode in presence of diverse metal ions were determined by the separate solution method; the observed values are presented in Table 1. For alkali and alkaline-earth metal ions, the K_{Zn,B}^{pot} values are of the order of 10⁻⁴ while the values lie in the range of 10⁻³ – 10⁻² for transition metal ions, except for Cu²⁺ and Pb²⁺ ions. It is usual to expect that ionophores containing sulfur donor atoms will have stronger interactions with Cu²⁺ and Pb²⁺ ions because of the relatively higher affinity of sulfur towards these cations. But, for the present electrode, the interference of these ions on the zinc ion response shows a lower value than expected, i.e., 6 to 9 in K_{Zn,B}^{pot} value. The reason for the anticipated selectivity of the Zn²⁺ membrane electrode over Cu²⁺, Pb²⁺ and other transition metal ions may be the fact that the relative stabilities of the metal complexes of the ionophore is largely affected by the steric hindrance determined by the length of the methylene chain in the C-shaped cavity in TBDTS molecule. Since Cu²⁺ and Pb²⁺ ions interfere with the response of zinc electrode, the presented electrode appears suitable for analysis of a zinc electroplating bath, because the anode used in zinc electroplating does not contain these metal ions in appreciable amounts. However, the zinc response is seriously interfered with by small amounts of Hg²⁺ and Ag⁺ ions; so these two ions must be removed before the analysis of zinc if the bathing solution or the plate contain mercury or silver. It is important to note that the selectivity coefficients for the Zn²⁺ electrode, with reference to most of the alkali and alkaline-earth metal ions, are quite small. This means that the membrane electrode based on TBDTS will be highly efficient for determination of trace amounts of zinc in the presence of a large excess of alkali and alkaline-earth metal ions. On the basis of the results discussed in this paper, we conclude that TBDTS is an important neutral carrier type ionophore that can be used for fabrication of Zn²⁺-selective electrodes. Such an electrode is expected to be suitable for applications to the measurement of zinc in electroplating processes and industrial effluents.

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References


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