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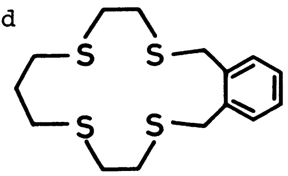
A PVC MATRIX MEMBRANE COPPER ION-SELECTIVE ELECTRODE BASED ON A MACROCYCLIC POLYTHIAETHER

Satsuo KAMATA,* Morihide HIGO, Takashi KAMIBEPPU,
and Ichiro TANAKA
Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890

The polyvinyl chloride (PVC) membrane electrode based on the macrocyclic polythiaether, 13,14-benzo-1,4,8,11-tetrathiacycropentadecane (TTX), exhibits the Nernstian behavior to the copper ion. The response time is rapid (< 20 sec) and the detection limit is of the order of 10^{-5} M.

Neutral carrier electrodes based on macrocyclic polyethers show high preference for alkali and alkaline earth metal cations.$^{1)}$ The selectivity for potassium of some electrodes is close to that of electrodes based on valinomycin. Macrocyclic polythiaethers have the ability to form complexes with transition metal cations. The thiaethers are expected, therefore, to be new sensor materials for these cations, but no attempt has been made to confirm it.$^{2)}$ In this letter, we have prepared the PVC membrane electrode based on TTX and have shown its usefulness to the copper ion.

TTX was synthesized from 1,3-propanedithiol, 2-chloroethanol and α,α′-dibromo-o-xylene by using the method described by Rosen and Busch.$^{3)}$ Recrystallization of the product from chloroform-ethanol mixtures and diethyl ether gave white needles. The structure was proven by elemental analysis, the nmr and the ir spectra.



TTX

The PVC membrane electrode was prepared as reported.$^{4)}$ TTX (30 mg), dioctylphthalate as plasticizer (120 mg) and PVC (240 mg) were dissolved in tetrahydrofurane (6 ml). The mixture was poured into a glass casting ring of 30 mm diameter and left for two days at 30°C to allow the solvent to evaporate. A disc of 6 mm diameter of thus obtained membrane of about 0.2 mm thick was cut with a cork-borer and fixed to a PVC tubing. Before use the electrode was soaked in 10^{-3} M $CuCl_2$ solution for one day; the electrode was also stored in this solution. The electrochemical cell is as follows:

Ag; AgCl | 10^{-3} M $CuCl_2$ | PVC membrane | Sample | Reference electrode.

All emf measurements were made relative to an Orion 90-01 reference electrode at 25°C with an Orion 901 ionalyzer. The response time was determined by rapidly changing the activity by introducing a more concentrated copper solution.

A typical calibration curve is shown in Fig. 1. The electrode exhibited the Nernstian behavior over the activity range of 10^{-1} to 10^{-4}; the slope was 28 mV and the detection limit near 10^{-5} M. The time required to achieve within 1 mV of the equilibrium potential value for changing concentration of 10^{-3} to 10^{-2} M was less than 20 sec.

TTX was found to be a useful sensor material for the copper ion. The electrode with this sensor has a rapid response and good potential stability; its property is comparable to that of the commercial solid-membrane copper-electrode. This letter is the first report on the transition metal ion-selective electrode based on a macrocyclic polythiaether. The thiaether may also be a useful sensor for other transition metal ions. Further investigations on the properties of this electrode to the copper ion and other metal ions are now in progress.

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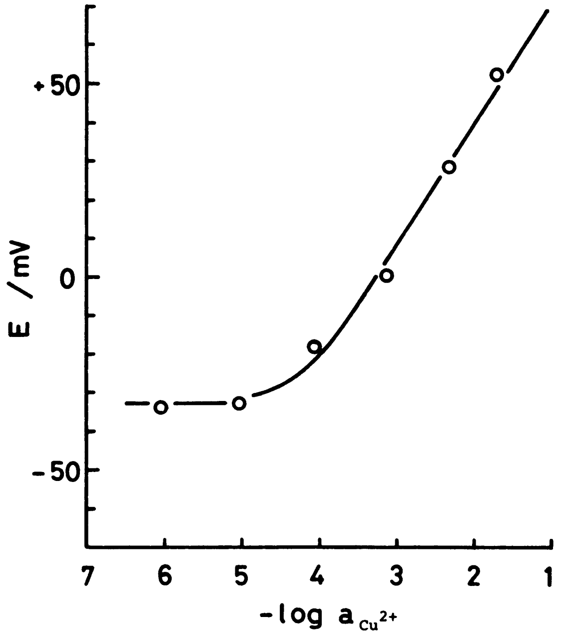

Fig. 1. Calibration curve for the PVC membrane copper-electrode using TTX.

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