CHEMISTRY LETTERS, pp. 533-534, 1987.

Xylene Bis(diethyldithiocarbamate) as a Neutral Carrier for Copper(II)-Selective Membrane Electrode

Satsuo KAMATA,* Fumiuki OGAWA, and Masaomi FUKUMOTO
Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890

Polyvinyl chloride (PVC) membrane electrode based on o-xylene bis(diethyldithiocarbamate) which was newly synthesized as a neutral carrier, exhibits a Nernstian behavior to copper(II) ion for activity range of 10^{-1} M to 10^{-5} M. The electrode has given good response for the time and selectivity.

Macrocyclic polythiaethers are known to be useful neutral carriers for a copper(II)-selective membrane electrode.[1] It is also well known that diethyldithiocarbamate forms complexes with many metals as a nonselective complexing agent.[2,3] The present study was undertaken with a view to investigate how far the substitution of a xylene group affects the nature of the dithiocarbamate. It is expected that this type of compound forms complexes with transition metals selectively because of the appropriate position of two dithiocarbamate radicals.

In this letter, we have synthesized o-xylene bis(diethyldithiocarbamate) (o-XBDEDTC) as a new neutral carrier and have shown its usefulness to a copper(II) ion sensor.

Synthesis of the reagent is as follows. Sodium N,N-diethyldithiocarbamate (0.1 mol) was dissolved in ethanol (500 ml) and α,α'-dibromo-o-xylene (0.05 mol) was added slowly to the solution under reflux with stirring. After keeping the same condition for 4 hours, the resultant precipitate was filtered, washed successively with water, and crystallized with ethanol to give white needle crystals (mp 80-81 °C). From the elemental analysis, IR, NMR, and MS, the structure of o-XBDEDTC was recognized as shown in Fig. 1.

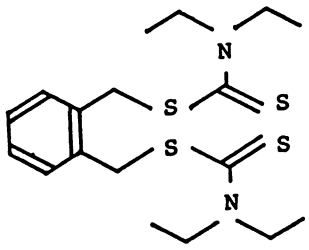

Fig. 1. o-XBDEDTC.

The membrane electrode was prepared as reported.[4] o-XBDEDTC (35 mg), o-nitrophenyloctylether (250 mg) as a plasticizer and PVC (250 mg) were dissolved in tetrahydrofuran (6 ml). The solution was poured into a glass cashing ring of 35 mm diameter on a glass plate and kept for two days at 30 °C. A membrane disc of 6 mm diameter was fixed to PVC tubing. The electrode was soaked in 10^{-3} M (1 M = 1 mol dm^{-3}) solution of $CuCl_2$ for a day. The electrochemical cell is as follows:

Ag; AgCl / 10^{-3}M $CuCl_2$ / sensor membrane / sample solution / reference electrode.

All emf measurements were made relative to a DKK Ag/AgCl reference electrode Type 4400 at 25 °C with an Orion 901 ionalyser.

A typical calibration curve exhibited Nernstian linear response with an activity range of 10^{-1} M to 10^{-5} M. The properties of the electrode are summarized in Table 1. Selectivity coefficients measured using the mixed solution method with a fixed level of interferents are comparable to those of a commercial solid-membrane copper(II)-selective electrode. Thus, o-XBDEDTC was found to be a useful sensor material of copper(II) ion. This material may also be a useful sensor for other transition metal ions. Futher investigation on the properties of this electrode to the copper and other metal ions are now in progress.

The authors thank Professor N.Ishibashi of Kyushu University and University Reader J.D.R.Thomas of UWIST (UK) for their encouragement.

Table 1. Properties of Cu(II)-selective membrane electrodes

Property	PVC membrane o-XBDEDTC	Solid membrane commercial [c]
Detection limit for Cu^{2+} (M)	2.5×10^{-7}	3.2×10^{-7}
Slope (mV/decade)	28	29.5
Response time (s) [a]	30	20
Effective pH range [b]	4.8-6.7	3.1-6.5
Selectivity coeffecient ($K^{pot}_{Cu,M}$)		
Mg^{2+}	1.4×10^{-3}	1.6×10^{-4}
Ca^{2+}	5.0×10^{-4}	1.1×10^{-4}
Cd^{2+}	7.9×10^{-3}	6.4×10^{-4}
Co^{2+}	3.7×10^{-3}	2.3×10^{-4}
Ni^{2+}	1.1×10^{-3}	3.2×10^{-4}
Mn^{2+}	4.8×10^{-3}	1.2×10^{-4}
Na^{+}	49	3.7×10^{-2}

a) Time required to obtain steady potential within 1 mV fluctuation for 10^{-3} M to 10^{-2} M solutions.
b) 10^{-3} M $CuCl_2$ solution.
c) TOA Electronics Ltd.

References

1) S.Kamata, M.Higo, T.Kamibeppu, and I.Tanaka, Chem. Lett., 1982, 287.
2) G.D.Thorn and R.A.Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., Amsterdam-New York (1962), pp. 157-164.
3) E.B.Sandell and H.Onishi, "Photometric Determination of Traces of Metals General Aspects," 4th ed of Part I of Colorimetric Determination of Traces of Metals, Jhon Wiley & Sons, Inc., New York (1978), pp. 512-532.
4) A.Craggs, G.J.Moody, and J.D.R.Thomas, J. Chem. Educ., 51, 541 (1974).

(Received December 11, 1986)