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Thiuram Monosulfides as a Neutral Carrier for Copper(II)-Selective Membrane Electrode

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Poly(vinyl chloride) membrane electrodes that are sensitive and selective to copper(II) ion were developed. The electrodes based on tetramethyl, tetraethyl and dipyrrolidine thiuram monosulfides as a neutral carrier, exhibit a Nernstian behavior to copper(II) ion in the activity range of 10^{-1} M to 10^{-6} M - 10^{-8} M. Properties of the electrodes are briefly discussed.

Ion-selective electrodes based on neutral carrier ligands have recently been investigated for copper(II) ion. In this respect, macrocyclic polythiaethers[1,2] and nonmacrocyclic bis type compound[3] have been prepared, and successfully used as ionophore in copper(II)-selective membrane electrode. These types of compounds selectively form complexes with transition metal cations. It is also found that the nonmacrocyclic bis type compound is a quite versatile chelating agent over macrocyclic polythiaethers. Taking this into account, we thought it interesting to observe characteristics of donor sulfur atoms by reducing the size of noncyclic cavity. Thiuram monosulfides, which have C-shaped cavities, are expected to selectively form complexes with transition metal cations. We therefore have used thiuram monosulfide as a sensor material for copper(II) ion.

In this letter, we report on a sensing system involving tetramethyl thiuram monosulfide (TMTMS), tetraethyl thiuram monosulfide (TETMS) and dipyrrolidine thiuram monosulfide (DPrTMS) used as a neutral carrier for copper(II)-selective membrane electrodes.

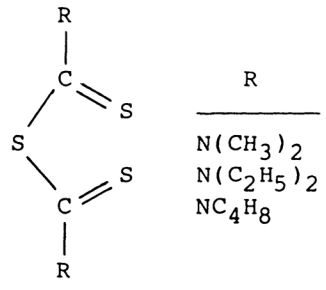

Fig.1. Thiuram monosulufide.

TMTMS was obtained from Nakarai Chemicals, Ltd. and used after twicely recryatallized with ethanol. TETMS and DPrTMS were prepared by the reported procedure.[4] Sodium salts of diethyl and pyrrolidine dithiocarbamates were oxidized with an aqueous solution of hydrogen peroxide and sulfuric acid mixture in the presence of cyanide ion. The final products were filtered, washed, dried and crystallized with ethanol. Melting points of TETMS and DPrTMS were found to be 33-34 °C and 104-106 °C, respectively. The purity of the compounds was checked by elemental analysis, IR, NMR and MS. The structure of the used ionophore is shown in Fig.1.

The preparation of the membrane was similar to the one reported earlier.[5] The ionophore, o-nitrophenyloctyl ether (NPOE) as a plasticizer, and poly(vinyl chloride) (PVC) were dissolved in 5 ml tetrahydrofuran (THF). The sensor polymeric

membranes were prepared by 5.2 or 7.1 wt% for TMTMS, TETMS or DPrTMS, 51 to 54 wt% for NPOE and 40 to 41 wt% for PVC. In case of DPrTMS ionophore membrane, 1 wt% sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTBTFPB) as a lipophilic anion excluder was used. The electrodes were conditioned before use by soaking for 24 h in 10^{-3} M (1 M = 1 mol dm^{-3}) of $CuCl_2$ solution. All the emf observations were made relative to a DKK Ag;AgCl reference electrode type 4400 at 25 °C with a Corning Digital 112 Research pH Meter. A typical calibration curve exhibited near Nernstian linear response with an activity range of 10^{-1} M to 10^{-6} M - 10^{-8} M for TMTMS, TETMS and DPrTMS, respectively. The properties of the electrodes are summarized in Table 1.

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

Electrode	1	2	3[a]
Ionophore	TMTMS	TETMS	DPrTMS
Detection limit/M	3.1×10^{-6}	2.5×10^{-8}	1.8×10^{-7}
Slope/mV per decade	31	31	26
Response time/s[b]	3	18	19
pH range[c]	4.5-6.5	3.4-6.6	3.5-5.7

a) NaTBTFPB was added, as lipophilic anionic site.
b) Time required to obtain steady potential within 1 mV fluctuation for 10^{-3} M to 10^{-2} M solutions.
c) 10^{-3} M $CuCl_2$ solution.

The selectivity coefficient values for different cations were determined by the mixed solution method.[5] The best available electrode based on ionophore TETMS rejected the interference of alkali and alkali earth, transition metal cations by a factor 10^2 and 10^3, respectively. The electrode based on DPrTMS exhibited the Nernstian lineality with activity range of 10^{-1}-10^{-4} M, even though the chloride ion of 10^{-1} M was contained in the solution. On the basis of the above results, it is confirmed that donor sulfur atoms with C-shaped cavity of thiuram monosulfide selectively form complexes with copper(II) ion. Thus, thiuram monosulfides such as TMTMS, TETMS and DPrTMS were found to be useful neutral carrier sensor materials for copper(II) ion.

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