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Methylene Bis(diisobutyldithiocarbamate) Neutral Carrier as Lead Sensing Material

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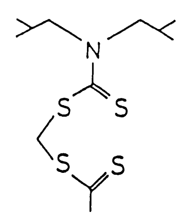
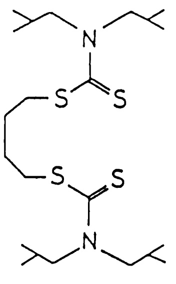
The sensitive and selective electrodes for lead(II) ion were developed by using the membrane based on methylene bis(diisobutyldithiocarbamate). The membrane electrode exhibited good response for Nernstian slope(28 mV/decade), linearity range(10^{-2}-10^{-6} M) and selectivity factor of different metal ions, except for copper(II) ion.

Much interest has recently been paid to the ionophore ligands as sensing materials for neutral carrier type ion-selective electrodes due to the unique properties of the compounds. The lead ion-selective electrodes have been investigated by using ionophores such as oxa- and dioxa-dicarbamides for monovalent(PbX^+) ion,1) and dibenzo-18-crown-6 and its derivatives for Pb^{2+} ion2-4) which are of oxygen donor atoms. It is well known that the sulfur ligands coordinate with transition and heavy metal ions to form complexes. The ionophores with sulfur donor atoms have previously been examined for copper(II) ion-selective electrodes.5-8) Therefore, this type of ionophore would also be expected to be used as sensing material for lead ion-selective electrode, because modifying the molecular structure of these ligands to improve ion selectivity is possible. In this letter, we have synthesized the lipophilic methylene bis-(diisobutyldithiocarbamate)(MBDiBDTC) and tetramethylene bis(diisobutyldithiocarbamate)(TMBDiBDTC) as new neutral carriers and have shown MBDiBDTC's usefulness as a lead(II) ion senior.

Synthesis of the ionophore is as follows. Diisobutylamine(140 mmol) and isopropanol(25 ml) were dissolved in water(300 ml) containing sodium hydroxide(140 mmol). This mixture was stirred at room temperature while carbon disulfide(140 mmol) was slowly added to the solution and allowed to react for 2 h. Precipitated sodium N,N'-diisobutyldithiocarbamate was filtered and crystallised from isopropanol, yield 64%, mp 36-37 °C. The recrystallized sodium N,N'-diisobutyldithiocarbamate(50 mmol) was dissolved in ethanol(300 ml) and methylene dibromide(25 mmol) was added slowly to the solution while refluxing and stirring for 7 h. The final compound, MBDiBDTC, was obtained as white crystals and recrystallised from ethanol, yield 5.1 g, 60%, mp 69-70 °C. TMBDiBDTC was synthesized by reacting sodium N,N'-diisobutyldithiocarbamate(40 mol) with tetramethylene dibromide(0.02 mol) in ethanol for 5 h, yield 6.4 g, 56%, mp 80-81 °C. The purity of the compounds was checked by elemental analysis, IR, NMR and MS. The method for preparing PVC immobilized ionophore membrane has been described previously.$^{5)}$ Ionophore(45 mg), o-nitrophenyloctyl ether(200 mg) as a plasticizer, potassium tetrakis(p-chlorophenyl)borate(3 mg) as an anion excluder and poly(vinyl chloride)(PVC)(150 mg) were dissolved in 5 mL of tetrahydrofuran(THF). 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 make a sensing membrane. The membrane electrode was made from fixing a disk(6 mm diameter) of the membrane to the PVC tubing. The electrodes were then soaked in a 10^{-3} M(1 M = 1 mol/dm^3) solution of lead nitrate solution for a day before use. All emf measurements were performed with the following electrochemical cell assembly: Ag-AgCl/ 10^{-3} M $PbCl_2$/ sensor membrane/ sample solution/ reference electrode. A Corning digital research pH meter(Model 112) was used for measuring the potential. The emf observations were made relative to a saturated calomel electrode(Iwaki Glass) in solutions stirred with a magnetic stirrer. The performance of the electrodes was examined by measuring the emfs of the lead nitrate solutions prepared with a concentration range of 10^{-1}-10^{-8} M by serial dilution. The activities of metal ions were based on activity coefficient(γ) data calculated from the modified form of the Debye-Hückel equation:



MBDiBDTC



TMBDiBDTC

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

where μ is the ionic strength and z the valency. All the measurements were carried out at 25 ± 0.1 °C. All the metal nitrate solutions were freshly prepared by dilution from their stock standard solution of 0.1 M with distilled, de-ionized water.

The membrane electrode with MBDiBDTC exhibited a Nernstian slope of 28 mV per decade with straight line between 10^{-2} and 10^{-6} M $Pb(NO_3)_2$. On the other hand, the membrane electrode with TMBDiBDTC showed a linearity range of 10^{-1} to 10^{-5} M $Pb(NO_3)_2$ which was shifted to a higher concentration than that of MBDiBDTC electrode. It is considered that the sensitivity of ionophore for lead ion is related to the size of its C-shaped cavity with sulfur donor atoms. This indicates that the MBDiBDTC ligand has an ideally sized C-shaped non-cyclic cavity to fit the lead ion.

The pH response profiles for electrodes were examined by using 10^{-3} M $Pb(NO_3)_2$ solution, adjusted with nitric acid(0.1 M) and sodium hydroxide (0.1 M) as acidic and alkaline media. Each electrode gave a useful pH range of 3.1-5.5. The influence of the pH response of the electrodes showed that the potential decreased at above pH 5.5, due to the formation of lead hydroxide in solution, while at a lower pH, potential increased, due to its response to the hydrogen ion. The response time of the electrode was tested by measuring the time required to achieve a level within 1 mV of a steady-state potential under constant stirring and rapidly increasing the solution concentration[9)] by 10 fold from 10^{-3} to 10^{-2} M. The electrodes based on MBDiBDTC and TMBDiBDTC achieved a steady potential within 16 and 8 s. That the response time of TMBDiBDTC for the lead ion is a little faster than that of MBDiBDTC, is probably related to the rate of complex formation.

The selectivity coefficients($K^{pot}_{Pb,B}$) of each electrode for various cations were evaluated by the mixed solution method,[9,10)] with a fixed concentration of interferent B in $Pb(NO_3)_2$ solutions of 10^{-1}-10^{-8} M. The electrode properties and the selectivity coefficient values are summarized in Table 1.

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

Ionophore	MBDiBDTC	TMBDiBDTC
Detection limit/M	3.5×10^{-7}	7.9×10^{-6}
Slope/mV per decade	28	29
Response time/s	16	8
pH range[a)]	3.1-5.4	3.5-5.4
Selectivity coefficient[b)]		
B	1)$K^{pot}_{Pb,B}$	2)$K^{pot}_{Pb,B}$
Mg^{2+}	5.5×10^{-6}	3.1×10^{-3}
Ca^{2+}	3.6×10^{-6}	4.1×10^{-3}
Mn^{2+}	6.2×10^{-6}	7.0×10^{-3}
Co^{2+}	6.3×10^{-6}	1.4×10^{-2}
Ni^{2+}	1.1×10^{-5}	1.6×10^{-2}
Cd^{2+}	2.7×10^{-4}	2.9×10^{-2}
Zn^{2+}	3)3.3×10^{-4}	3.1×10^{-2}
Cu^{2+}	4)5.3	4)1.3×10
Na^{+}	2)7.4×10^{-3}	4.9×10^{-2}
Fe^{3+}	3)2.9×10^{-3}	---

a) 10^{-3} M $Pb(NO_3)_2$ solution.

b) Concentrations of interferent(B) are 1) 1.0×10^{-1} M, 2) 1.0×10^{-2} M, 3) 1.0×10^{-3} M, 4) 1.0×10^{-5} M.

Both electrodes based on the MBDiBDTC and TMBDiBDTC were strongly interfered with the copper(II) ion. This means that both ionophores with four sulfur atoms form complexes with copper(II) ion easily due to strong interaction of copper(II) with sulfur, regardless of the different distances between two dithiocarbamate groups on MBDiBDTC and TMBDiBDTC. The MBDiBDTC membrane electrode showed better selectivity factors for the other different metal cations than that of the TMBDiBDTC membrane electrode. This means that the coordination or uptake of lead ion by ionophore ligand is mainly related to the size of the C-shaped cavity of ligand to fit lead ion, due to lead ion coordinating weakly with the donor sulfur atom compared with copper(II) ion. The MBDiBDTC membrane showed therefore good selectivity having an ideal sized C-shaped cavity for lead ion. On the other hand, TMBDiBDTC has a long distance and free rotation between two dithiocarbamate groups linked by the four linear carbon chains of the ligand molecule and also has a large C-shaped cavity. Therefore the selectivities for TMBDiBDTC membrane were not so good, because the lead ion is loosely coordinated with TMBDiBDTC ligand and exchanged easily with different metal ions. The membrane electrode based on MBDiBDTC responded to the lead (II) ion and showed good sensitivity properties and selectivities in comparison to the membrane with dibenzo-18-crown-6 ionophore.$^{4)}$ Except for copper(II) ion, the selectivity of different cations for the membrane electrode with MBDiBDTC exhibited nearly the same tendency as the lead-selective electrode based on dioxadicarbamide compound, which responded to the monovalent lead ion, PbX^-.

Therefore, MBDiBDTC is a good sensor material for the lead(II) ion due to the ideal size of the C-shaped cavity of the compound fitting the lead ion.

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