Neutral 1,4-Bis(3-thiapentylxanthato)butane as Sensing Material for Samarium(III) Ion

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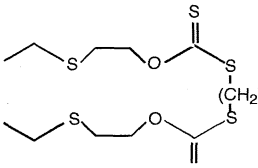
Membrane-coated carbon rod electrodes were constructed by incorporating 1,4-bis(3-thiapentylxanthato)butane as the active ionophore. These electrodes exhibited near Nernstian responses with a slope of 19.7 mV per decade of concentration change, toward samarium(III) ion. The observed detection limit for determination of Sm(III) was 5×10^{-7} M (1M=1 mol dm^{-3}) in aqueous solutions. The selectivity coefficients of the electrode against a number of diverse ions are discussed.

The growing industrial use of rare earth metals calls for an immediate development of a simple and convenient method of rare earth analysis in solution. In this respect, a number of rare earth selective electrodes have been reported. These electrodes are either based on solid-state sensors containing rare earth oxides,[1-3] or contain conventional liquid ion exchangers derived from dinonyl naphthalene sulfonic acid,[4] di(2-ethylhexyl) phosphoric acid,[5] and tributylphosphate.[3] Some of those electrodes are reported to be highly sensitive to particular rare earth ions but often suffer from the lack of the required range of linearity and selectivity for determination of individual rare earth ions in multi-component solutions. Rare earth-selective electrodes based on neutral carrier ionophore are not yet reported. In our laboratory, we have prepared a number of neutral ionophores composed of the bis derivatives of thia-alkyl xanthates. These open chain compounds contain SOSSOS donor sets in a highly flexible structure, which were expected to act as active ionophores for rare earth ions through weak coordination by OS donor atoms, as was seen in the formation of lanthanoid(III) complexes of polythia macrocycles of 18-crown-6 type.[6] In this article, we report the new type of Sm(III)-selective electrodes based on 1,4-bis(3-thiapentylxanthato)butane.



ionophore **1** : n=3

ionophore **2** : n=4

The reaction of 3-thiapentylxanthate (potassium salt) with dibromopropane or dibromobutane afforded the bis(3-thiapentylxanthato)alkanes. The purified compounds appeared as faintly colored liquids possessing boiling points >200 °C and specific gravity values near to 1.1. These compounds were identified by the elemental analysis, infrared and ^{1}H NMR data.[12] Stock solution of Sm(III) ion (10^{-1} M) was prepared by dissolving $Sm(NO_3)_3.6H_2O$ (99.5% purity) in distilled, de-ionized water and working solutions were obtained by serial dilution. All other chemicals used in the analytical determinations were of the highest available purities. The PVC membrane of the sensor was immobilized on a carbon rod of 4 mm diameter in a manner described in an earlier publication.[7] The usual composition of the membrane was: Ionophore **1** or **2**, 10.2 wt%; PVC, 28.7 wt%; the plasticizer, o-nitrophenyl octyl ether (NPOE), 60.4 wt% and potassium tetrakis(4-chlorophenyl)borate (KTCPB), 0.7 wt% used as the anion excluder. EMF measurements for the Sm(III) electrodes were performed with a cell assembly of the type : Membrane-coated carbon rod electrode / sample solution / saturated calomel electrode (as the reference). Nominal pH value of 5.5 was maintained for the analyte solutions where the cell EMF was recorded after well mixing of the components at 25±2 °C. The activities of the metal ions in the analyte solutions were calculated from their activity coefficient values as given by the modified Debye-Hückel equation.[8] The analytical performances of the membranes prepared with each of the ionophores (compounds **1**,**2**) were evaluated by their EMF vs. $a_{Sm(III)}$ data.

Initial experiments were carried out to evaluate the response of the ionophores presented in this article towards Sm(III) ion. For this, a series of electrodes were constructed by incorporating the ionophores **1** and **2** separately in the membrane medium. The EMF values produced by these electrodes were recorded in $Sm(NO_3)_3$ solutions where the concentration of the Sm(III) ion was varied from 10^{-9} to 10^{-2} M. The analytical performances observed with both ionophores are summarized in Table 1. The experimental data show that the ionophore **2** (n=4) provides much better electrode for samarium determination than that given by ionophore **1** (n=3). This may be attributed to the fact that the greater size of the ligand cavity in the ionophore **2** (n=4) facilitates the easier adaptation and quicker release of the Sm(III) ion compared to those with the membrane of **1**. Both the electrodes exhibited slope values near to 19.5 mV per decade change of Sm(III) concentration which are very close to an ideal Nernstian response for the uptake of a trivalent cation into the carrier membrane. The Sm(III) electrode with 1,4-bis(3-thiapentyl-xanthato)butane (ionophore **2**) is characterized with a lower detection limit and shorter response time than those of the previously reported rare earth electrodes.[1-5] This is indicative of a better exchange of the trivalent cation between the flexible open chain structure of the neutral carrier in the membrane and the aqueous solution, compared to that operating in the cases of

Table 1. Properties of the Sm(III)-selective electrodes based on ionophores **1** and **2**

Ionophore	Slope(mV)	Detection Limit (M)	Response Time (s)	Linearity Range(M)
1	19.2	1×10^{-6}	12.0	5×10^{-3}~2×10^{-6}
2	20.0	5×10^{-7}	5.0	5×10^{-3}~1×10^{-6}

solid-state and ion exchanger type electrodes. Because of the better performances of ionophore **2**, the selectivity of Sm(III) determination was evaluated on the electrode containing 1,4-bis(3-thiapentylxanthato)butane. The potentiometric selectivity coefficient ($\log K_{\mathrm{Sm,B}}^{\mathrm{pot}}$) values are given in a logarithmic scale in Figure 1. These have been determined by the matched potential method[9] in which

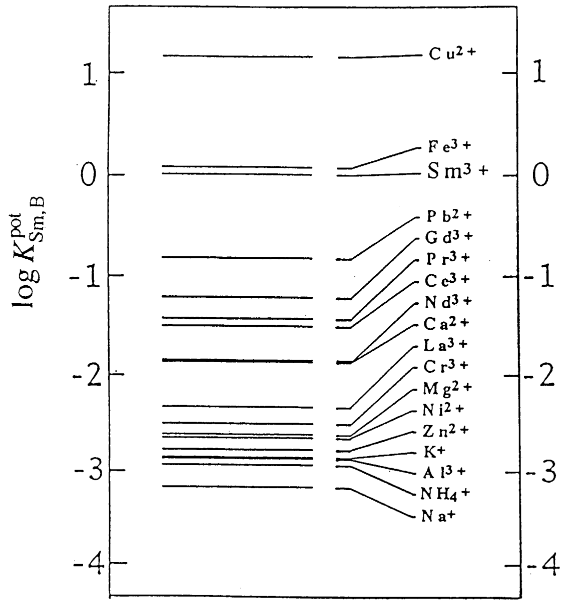


Figure 1. Selectivity coefficient ($\log K_{\mathrm{Sm,B}}^{\mathrm{pot}}$) values of Sm(III) electrode based on ionophore **2**.

the concentration of the interfering ions was varied in 10^{-5} M Sm(III) ion solutions. Monovalent cations (Na^+, K^+, NH_4^+) are rejected by the Sm(III) electrode by an order of about 10^3 or more. The selectivity coefficient values for divalent cations (Mg^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}) are in the range of -1.8 to -2.7, indicating that their presence will not hamper the determination of samarium. Selectivity against trivalent cations Al^{3+} and Cr^{3+} are also in the safe region. The most important property of the presented Sm(III) electrode is its selectivity against other rare earth cations. As seen in Figure 1, the $\log K_{\mathrm{Sm,B}}^{\mathrm{pot}}$ values for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Gd^{3+} fall in the range of -1.2 to -2.4, indicating that the ionophore having the bis(thia-alkylxanthato)alkane structure can differentiate between the individual rare earth ions. Such distinction was not possible with previously reported rare earth selective electrodes. The present electrode also shows good selectivity for samarium determination in the presence of the neighboring Nd^{3+} ion. The observed lanthanide selectivities of the presented electrodes can be explained in the light of the conventional idea of cation-cavity size relationship[10], assuming that both the ionophores can adopt a cavity like structure at the event of complexation with the metal ions. Nevertheless, other factors such as the membrane polarity contributing to the stability of the cation-ionophore complex play definite role to impose the observed cation selectivity. If we consider the lanthanide(III) ions under study, the ionic diameter(Å) increases in the order: Gd^{3+}(1.94) < Sm^{3+}(2.00) < Nd^{3+}(2.08) < Pr^{3+}(2.21) < Ce^{3+}(2.14) < La^{3+}(2.28). A molecular modeling estimation of the ionophores **1** and **2** shows that a separation of approximately 1.81 Å is possible between the two parallel chains containing the donor atoms in **1**. This distance varies from 2.29~2.61 Å in **2**, as defined by the allowed rotations along the bridging alkylene chain. If we make allowance for the actual bond lengths for Sm-S and Sm-O coordination[6], it appears that the most stable structural conformation in ionophore **2** provides the optimum cavity size to accommodate Sm^{3+} ion, whereas the other lanthanide(III) ions are rejected according as the deviation from this optimal condition. Thus, the observed selectivity pattern of the electrode with ionophore **2** may be attributed to the flexibility and the distribution of the donor atoms in the open chain structure. From the selectivity coefficient data, the major interferents in the determination of samarium are identified to be Cu^{2+} and Fe^{3+} and to some extent Pb^{2+}. Soft metal cations like Pd^{2+} and Au^{3+} may also produce interferences on the Sm(III) response. These ions have been found to produce interferences in other ion selective electrodes based on sulfur-ionophores[11] and must be removed prior to samarium analysis, preferably by the use of a suitable masking agent like sodium or potassium cyanide.

The rare earth sensitivity of two bis(thia-alkylxanthato)alkanes as neutral carrier ionophore in membrane electrodes has been presented in this article. Potentiometric data proves that the compounds having bis(thia-alkylxanthato)alkane structure are good sensing materials for samarium(III) ion. Further researches aimed at evaluating other ionophores of similar structure and at optimizing the relevant analytical parameters are in progress.

References and Notes

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12 Elemental analysis (EA) and ^{1}H NMR data for the synthesized compounds:- Ionophore **1**, EA (%), Found (Calcd) : C, 38.32 (38.58); H, 5.82(5.98), NMR, δ (ppm) = 1.298 (t, 7.2 Hz, 6H); 1.972 (q, 6.8 Hz, 2H); 2.619 (q, 6.7 Hz, 4H); 3.072 (t, 7.2 Hz, 4H); 3.179 (m, 7.2 Hz, 4H); 4.742 (t, 7.2 Hz, 4H) (total 24 protons).

Ionophore **2**, EA (%), Found (Calcd) : C, 40.13(40.16); H, 6.21 (6.26), NMR, δ (ppm) = 1.284 (t, 7.2 Hz, 6H); 1.730 (t, 6.6 Hz, 4H); 2.610 (q, 7.2 Hz, 4H); 2.744 (q, 6.8 Hz, 4H); 3.121 (t, 7.6 Hz, 4H), 4.729 (t, 7.2 Hz,4H) (total 26 protons). (in the NMR data, t = triplet, q= quadruplet and m = multiplet).