

# Physico-Chemical Investigations on the Complexation of Heavy Metal Ions with Dithiolterephthalic Acid

## Part IV Amperometric Study on the Complexes of Tl(I) Sm (III) and Pr (III)

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The amperometric titrations carried out between  $\text{Na}_2$ -dithiolterephthalate  $[\text{R}(\text{SNa})_2]$  and Tl(I), Sm(III) and Pr(III) at  $E_d.e. = -0.01$  V (VS S.C.E.) reveal the formation of insoluble compounds having the compositions, (I)  $\text{RS}_2\text{Tl}_2$ , (II)  $(\text{RS}_2)_3\text{Sm}_2$  and (III)  $(\text{RS}_2)_3\text{Pr}_2$ . The compounds of Sm (III) and Pr(III) have appreciable solubility and hence their reactions were studied in 50% aq.-ethanolic medium. Thallium (I)—dithiolterephthalate is sparingly soluble compound and its formation has also been substantiated conductometrically.

In earlier communications the authors have reported the electrochemical behaviour of dithiolterephthalate<sup>1</sup> and its interaction with various metal ions viz., Zn (II), Cd (II), Hg (II), Cu (II), Ag (I) and Pb (II)<sup>2-4</sup>. In the present investigation efforts have been made to study the course of reaction of Disodium dithiolterephthalate (referred to herein as  $\text{R}(\text{SNa})_2$  with heavy metal ions viz., Tl(I), Sm(III) and Pr(III). The literature is however silent regarding this study.

### Experimental

Current measurements were made using a Cambridge (General purpose) polarograph coupled with a dropping mercury electrode and saturated calomel electrode. The capillary had the following characteristics,  $m = 1.427$  mg/sec.,  $t = 3.62$  sec. and  $m^{2/3}/t^{1/6} = 1.571$   $\text{mg}^{2/3}/\text{sec}^{-1/6}$  at zero volts (vs. S.C.E.) in 0.1M  $\text{KNO}_3$ . Deaeration and stirring of solution were carried out by bubbling oxygen free nitrogen. All titrations were carried out at 25° maintained by electrically operated thermostat type  $U_3$  (German). Conductance measurements were made on a visual magic eye type conductometer using a cell fitted with platinised platinum electrodes.

Dithiolterephthalic acid was obtained from the Evan's Chematics, New York. All other chemicals were of Anal.-R. B.D.H. grade. Dithiolterephthalic acid is insoluble in water. A 0.1M stock solution of its disodium salt was prepared by digesting a known weight of dithiolterephthalic acid in a requisite amount of NaOH, which took 3-4 days.

### Results and Discussion

Authors have already reported<sup>1</sup> that the  $\text{R}(\text{SNa})_2$  depolarizes the mercury with the formation of an intermediate soluble mercurous compound which

rapidly changes into an insoluble mercuric complex. The anodic wave corresponds to the two electron oxidation process and was found to be diffusion controlled, whose height depends on the concentration of the depolarizer. The proportionality of the diffusion current with concentration and the limiting current plateau potential,  $-0.01$  volts vs. S.C.E., at which most of the heavy metal ions do not reduce, provide favourable conditions for performing amperometric titrations of metal ions.

In order to study the reactions of Tl(I); Sm(III) and Pr(III) with  $\text{R}(\text{SNa})_2$  a series of amperometric titrations were carried out using different concentrations of the reactants both by direct and reverse methods at  $E_d.e. = 0.01$  volts and in the presence of 0.25M  $\text{KNO}_3$  and 0.01% Triton X-100. Aliquots of titrant were added by means of a microburette and the observed currents after correction for dilution effect were plotted against the volume of titrant added and the end points were located graphically.

*Interaction with Tl(I):* Fig. 1 represents the typical titration curves between  $\text{R}(\text{SNa})_2$  and Tl(I). In case of direct titrations (Fig. 1, curve-I) when the increasing amounts of Tl(I) are added to  $\text{R}(\text{SNa})_2$  solution, the anodic limiting current produced by  $\text{R}(\text{SNa})_2$  remains constant instead of decreasing till about 1.3 mole of Tl per mole of ligand is added. This indicates that upto this point the reaction between the dithiol and the metal practically does not take place. Further addition of the Tl ions causes immediate interaction as a result of which anodic current decreases sharply, reaches to almost zero value at the equivalence point indicating the completion of the reaction. The further addition of Tl ions does not produce any appreciable change in the cathodic current. In case of reverse titrations (Fig. 1, Curve-II) addition of ligand to Tl solution

decreases the initial cathodic current slowly and gradually til the end point is reached, beyond which addition of the ligand produces anodic current which increases linearly. In both the cases the end points were obtained from the intersection of the titrant line with the galvanometer zero line, which suggest the formation of 1 : 2 complex. It is striking to note that when the metal ion is present in excess

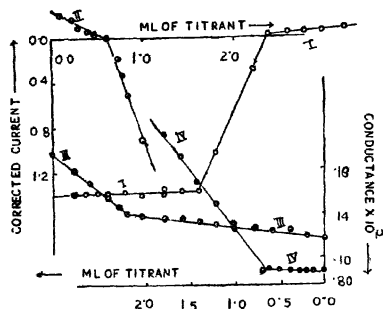


Fig. 1. Amperometric and conductometric titrations between Tl(I) and Na<sub>2</sub> dithiolterephthalate.

- Curve I  $\frac{M}{400}$  ligand vs. M/25 Tl(NO<sub>3</sub>)<sub>3</sub> } Amperometric
- II  $\frac{M}{400}$  Tl(NO<sub>3</sub>)<sub>3</sub> vs. M/25 ligand } Amperometric
- Curve III  $\frac{M}{400}$  ligand vs. M/25 Tl(NO<sub>3</sub>)<sub>3</sub> } Conductometric.
- IV  $\frac{M}{400}$  Tl(NO<sub>3</sub>)<sub>3</sub> vs. M/25 ligand. } Conductometric.

(inverse titration) the first addition of the ligand causes the formation of thallium-dithiolterephthalate but in presence of excess of ligand (direct titration) the reaction does not start immediately on the addition of the Tl. After the addition of more than 1.3 mole of Tl per mole of ligand the reaction starts and the free Tl and ligand, present in the cell change immediately into Thallium-dithiolterephthalate as indicated by a steep decrease in the anodic current. The reaction can be shown as follows :



The conductometric titrations were also carried out between R(SNa)<sub>2</sub> and Tl(I) (Fig. 1., Curve III and IV) which yield well defined breaks and the end points substantiate the results of amperometric study.

*Interaction with Sm(III) and Pr(III) :* Amperometric titration curves with Sm(III) and Pr(III) have been shown in Fig. II. When Sm(III) ions are added (direct titrations Fig. 2, curve 1) to the R(SNa)<sub>2</sub> solution, the initial anodic current produced by the ligand decreases to a lesser degree but on further addition sharp decrease is observed. After the addition of 0.66 moles of Sm per mole of ligand and anodic current increases again. This abnormal shape of the direct titration curve may be ascribed to the absence of reaction in the beginning because

of the insufficient amount of Sm(III) as compared to large excess of ligand. The increase in the anodic current after the end point may be due to the increase in solubility of the compound, on the addition of free metal ion.

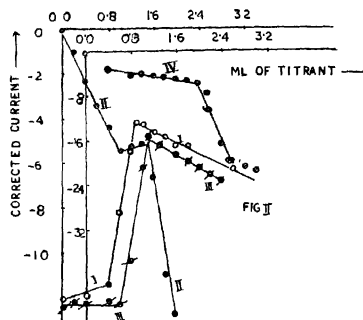
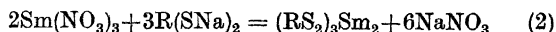


Fig. II. Amperometric titrations between Sm(III), Pr(III) and Na<sub>2</sub> dithiolterephthalate.

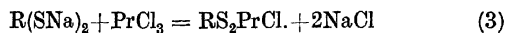
- Curve I M/250 ligand vs. M/25 Sm(NO<sub>3</sub>)<sub>3</sub>.
- II M/250 Sm(NO<sub>3</sub>)<sub>3</sub> vs. M/25 ligand.
- III M/250 ligand vs. M/25 PrCl<sub>3</sub>.
- IV M/250 PrCl<sub>3</sub> vs. M/25 ligand.

Reverse titrations (Fig. II, curve II) substantiate the shape of direct titration curves. Samarium ions do not reduce at the potential at which titrations have been carried out, hence no current has been shown initially by Sm(NO<sub>3</sub>)<sub>3</sub>. When the ligand which produces anodic current at the applied potential, is added, the anodic current increases gradually instead of remaining unchanged, showing the presence of free ligand. Further addition, beyond one mole of ligand per mole of Sm, does not change the anodic current till 1.5 moles of ligand per mole of Sm are added. After this point i.e. the end point, the current increases sharply with the addition of ligand. The end points given by direct and reverse titrations indicate the interaction of metal and ligand in the ratio = 2 : 3 according to the following equation :



The interaction of Pr(III) with R(SNa)<sub>2</sub> is very interesting. The shape of the amperometric titration curves is almost identical with those of Sm(III). In presence of excess of ligand (direct titrations) (Fig. II, curve III) praseodymium reacts in a similar manner forming similar compounds as formed by Sm(III). But the reaction of R(SNa)<sub>2</sub> in presence of initial excess of metal (reverse titrations Fig. 2, curve IV) is different. When ligand is added to PrCl<sub>3</sub> solution the current does not increase initially, as in the case of Sm, but it changes gradually till one mole of ligand per mole of metal is added, after which the anodic current increases linearly with the addition of ligand, thus showing the presence of free ligand. It can, therefore, be inferred that the reaction stops after the addition of 1 mole of ligand per mole of Pr(III). Hence, when the metal

is present in excess a different compound is formed as follows :



The amperometric titration curves are quite typical; they appear abnormal in shape but show that the inner transition elements, Sm(III), and Pr(III), react with  $R(SNa)_2$  in a very interesting way. It is difficult to follow their reactions in pure aqueous medium as the compounds formed have fairly good solubility. The reactions were therefore carried out in 50% aqueous ethanolic medium, which made it possible to explore the reactions between  $R(SNa)_2$  and Sm(III) and Pr(III).

The change of ionic strength and amount of ethanol beyond 50% has no appreciable effect on the shape of titration curve and the end points. Well defined curves are obtained with concentrated solutions of

reactants. Dilute reactants (concentration < 1 mM) do not provide dependable and reproducible results.

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