Polarographic Studies on Lead-Tris Complexes and Determination of Pb^{2+}, Tl^{+} and Te^{2+} in Binary Mixtures

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The reduction of Pb^{2+} in tris medium at d.m.e in presence of 0.1 M KNO has been found to be reversible and diffusion controlled. The plot of $-E_{1/2}$ vs -log [Tris] revealed the successive formation of metal - Tris complexes. The stepwise formation constants of these complexes have been determined at 26 ± 0.1°C employing DeFord and Hume's method. The polarographic studies of Tl^{+} and Te^{4+} in Tris have been reported for the first time. Simultaneous determination of Pb^{2+}, Tl^{+} and Te^{4+} in binary mixtures have also been carried out.

Tris (hydroxymethyl) methylamine (Tris) has been used primarily as buffering medium in many biochemical applications and as a titrimetric standard in potentiometry(2). The interference of metal ions was noticed in the reactions where Tris is used as buffer(3). The polarographic behaviour of Tris with copper has been studied(4). Simultaneous determination of Cu^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} in ternery and quarternary mixtures using Tris are reported (5,6). Brigane et al (7) studied Pb - Tris and Cd - Tris complexes in sodium perchlorate medium polarographically at low concentrations of Tris. The present communication is the reinvestigation of the complexation of Tris with lead polarographically at higher pHs and at higher concentrations of Tris in a different supporting electrolyte (0.1 M KNO_3). The studies of Tl^{+} and Te^{4+} in Tris are made for the first time. The determinations Pb^{2+}, Ti^{+} and Te^{4+} when present alone and in binary mixtures are reported.

EXPERIMENTAL

Tris (hydroxymethyl) methylamine of BDH sample was used. Metal ion solutions were prepared from AR grade samples. 0.1 M potassium nitrate (AR) solution was used to keep the ionic strength constant. 4% mannitol was used to supress the hydrolysis of Tris (9). Conductivity water was used in the preparation of all solutions. 0.002% Triton x 100 was used as maxima suppressor. All other chemicals used were of reagent grade. Purified nitrogen gas was used for the de-oxygenation of all working solutions prior to recording.

A CL-25 ELICO DC pen recording polarograph was used. Double distilled mercury was used for the dme. Sargent capillary (Sargent Welch & Co, USA) used for the dropping mercury electrode had a flow velocity of 2.546 mg/sec at 86 cm head of mercury and a drop time of 3.37 sec in conductivity water. SCE was used as the reference electrode. ELICO pH Meter was used to adjust the pH of the experimental solutions by adding nitric acid or sodium hydroxide as the case may be. The H-type cell of Lingane and Latimer was employed. The polarograms recorded at 26 ± 0.1°C.

RESULTS AND DISCUSSION

The polarograms of Pb^{2+}, Te^{4+} and Tl^{+} at dme yield single, well defined, cathodic waves in Tris at higher pHs (> 9.0). At any particular concentration of Tris, the increase of pH has a positive effect on the diffusion current and half-wave potentials in the case of Pb^{2+} and Te^{4+} and no effect with Tl^{+} Constancy of $id/\sqrt{h}$ indicates the diffusion controlled nature of the reduction wave in all the three systems. The plot of log $i(i_d - i)^{-1}$ vs $-E_{dc}$ yielded straight lines with slopes of 29 ± 2 mV in the case Pb^{2+}, 20 ± mV in the case of Te^{4+} indicating the reversibility and irreversibility of the electrode reaction involving two electron and four electron reduction processes respectively. The slopes of log plots and $E_{3/4} - E_{1/4}$ values revealed that the electrode reaction at dme was irrev ersible in the case of Tl^{+}.

The half-wave potentials shifted towards more negative value and diffusion current decreased with increasing Tris concentration indicating complexation of Pb^{2+}, Te^{4+} with Tris whereas diffusion current decreased and half-wave potential remained constant in the case of Tl^{+} indicating non-complexation.

A plot of $-E_{1/2}$ as a function of -log (Tris) showed the curvature indicative of the formation of successive complexes of Pb^{2+} with Tris and hence Deford and Hume's method was employed for determining the stabilities of different complexes. Fig. 1 shows the plot of $F_o[X]$, $F_1[X]$ and $F_2[X]$ vs ligand concentration. Extrapolation of these curves at $C_x = 0$ gave vlues of formation constants as $\beta_1 = 1.2 \times 10^4$; $\beta = 9.0 \times 10^5$. The plot of $F_2(X)$ vs C_x of Pb^{2+} - Tris system yielded straight line parallel to C_x axis which indicates

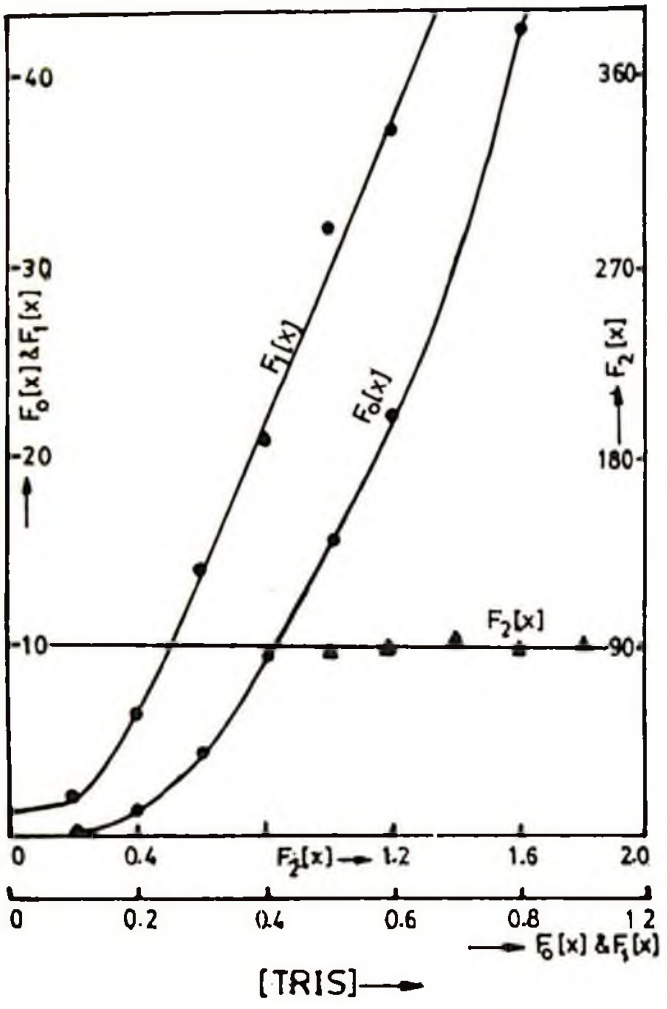


Fig. 1 Plots of F (X) vs [Tris] of Pb - Tris system at 26°C.

that the highest metal ligand ratio in the complex is 1:2 (Table 1).

ANALYSIS OF LEAD AND TELLURIUM

The half-wave potentials of lead (-0.58 vs SCE) and tellurium (-0.98 V vs SCE) were well separated from each other in 1.0 M KNO_3 and 1.0 M Tris at pH 10.5, thus enabling the simultaneous determination in a mixuture. Number of synthetic mixtures of these two metal ions were prepared and polarographed in the above mentioned medium. The measured wave heights of these solutions were computed from the calibration curves of metal ions. The results are presented in Table 2.

Polarograms recorded in the presence of 100-fold amounts of iron (II), cobalt (II), copper, nickel, manganese (II), chromium (VI) and sulphate, citrate, tartrate and oxalate revealed that these ions did not interfere in the determination. Thallium, cadmium, and zinc interfere when present in 50-fold.

ALALYSIS OF LEAD AND THALLIUM

Lead and thallium resemble each other in many of their chemical properties and their determination in a single operation by polarographic technique

TABLE 1

POLAROGRAPHIC DATA OF LEAD-TRIS SYSTEMS; [Pb] = 0.8 mM ; TRITON-X-100 = 0.002% [KNO] = 0.1 M ; pH = 10.5

S.No.	Concn of Tris M	Diffusion current i_d μ A	Slope mV	$E_{1/2}$ -V vs	ΔE	Log Im/Ic
1	0.00	6.1	29.7	0.410	0.000	0.00
2	0.02	5.9	33.3	0.434	0.024	0.01
3	0.04	5.9	32.7	0.448	0.038	0.02
4	0.08	5.6	32.5	0.472	0.062	0.03
5	0.10	5.4	32.3	0.508	0.098	0.05
6	0.20	5.2	32.1	0.530	0.120	0.07
7	0.30	4.7	30.0	0.544	0.134	0.11
8	0.40	4.5	31.3	0.552	0.142	0.13
9	0.50	4.3	29.8	0.560	0.150	0.15
10	0.60	4.2	29.7	0.564	0.154	0.16
11	0.80	4.1	29.5	0.572	0.162	0.17
12	1.00	3.6	29.0	0.580	0.170	0.22
13	1.20	3.5	29.7	0.584	0.174	0.24
14	1.40	3.2	29.0	0.588	0.178	0.28
15	1.60	3.1	29.5	0.590	0.180	0.30
16	1.80	2.7	29.8	0.592	0.182	0.35

$\beta_1 = 1.2 \times 10^4$ $\beta_2 = 9.0 \times 10^5$

TABLE 2

SIMULTANEOUS DETERMINATION OF LEAD AND TELLURIUM IN BINARY MIXTURES
[Tris] = 1.0 M ; Triton-X-100 = 0.002%
[KNO_3] = 0.1 M ; Sensitivity = 0.6
pH = 10.5

S.No.	Amount taken (mg)		Amount taken (mg)		Error %	
	Lead	Tellurium	Lead	Tellurium	Lead	Tellurium
1	10.06	9.57	10.06	9.73	0.00	+1.66
2	14.08	4.78	13.83	4.78	-1.78	0.00
3	15.08	6.38	15.08	6.38	0.00	0.00
4	16.09	3.19	15.84	3.25	-1.56	+2.00

is of considerable interest. Although the half-wave potentials of lead and thallium were very close in simple supporting electrolyte, determination of these are achieved on the basis of complex formation. Lead formed complexes with any concentration of Tris and at any pH studied giving rise to considerable shift in $E_{1/2}$ towards more negative values, whereas thallium did not form complex with Tris.

Synthetic solutions were prepared with lead and thallium in different ratios and polarographed. The concentration of the metal ions in the solutions were then calculated by computing the values of diffusion current with the calibration curves obtained from individual metal ions. The results obtained are presented in Table - 3

The presence of iron (II), chromium (VI), tellurium(IV), copper(II), nickel(II), cobalt(II), manganese(II), sulphate, citrate,tartrate, oxalate and Sulphate did not interfere in the determination of lead and thallium. However zinc and cadmium interfere when present in 50-fold excess.

TABLE 3

SIMULTANEOUS DETERMINATION OF LEAD AND THALLIUM IN BINARY MIXTURES
[Tris] = 2.0 M ; [KNO_3] = 0.1 M ; pH 12.0
Triton x 100 = 0.002%; Sensitivity = 0.08

S.No.	Amount taken (mg)		Amount found (mg)		Error%	
	Lead	Thallium	Lead	Thallium	Lead	Thallium
1	4.02	4.07	4.02	4.06	0.00	-0.04
2	5.03	2.03	4.96	2.03	-1.40	0.00
3	7.04	1.02	6.97	1.02	-1.00	+0.08
4	10.06	3.05	10.06	3.05	0.00	+0.04

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