Polographic Studies on Copper(I)-Schiff Base Complex and Determination of Copper in an Alloy

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The complexation of copper(II) with salicyladehyde tris (hydroxymethyl)methylamine (ST) has been investigated polarographically using 0.1 M KNO_3 supporting electrolyte. The stability constants of the two complexes are (β_1 = 7.5 x 10^7 and β_2 = 2.9 x 10^9) found to be higher than Cd-ST complexes (β_1 = 1.1 x10^6 and β_2 = 8.0 x 10^6). The concentration range studied for copper is 0.5 - 1.6 mM. The present method has been applied for the determination of copper in an alloy.

Schiff bases have theoretical and experimental significance in polarographic studies of metal ions. A survey of literature revealed that the synthesis(1) of salicylaldehyde tris (hydroxymethyl) methylamine (ST) and its ligational behaviour (1,2) towards some transition metal ions are reported by Rustagi and Rao. Polarographic(3) and potentiometric (4) studies on Cd-ST complex are also reported by Vyas et al. Potentiometric (4) and spectrophotometric(5) determination of copper using ST is known but the electrochemical behaviour of copper complexes of ST at DME and determination of copper has not been reported so far. In this paper polarographic characteristics of copper (II) complexes of ST have been investigated and suitable conditions have been suggested for the determination of copper when present alone and in an alloy.

EXPERIMENTAL

Reagents

Salicylaldehyde tris (hydroxymethyl)methylamine (ST)solution, 1 M.: The reagent was prepared according to the literature procedure (3) and the solution was made by dissolving in dimethylformamide.

Copper (II) solution, 1 x 10^{-2} M.: prepared from analytical reagent grade copper sulphate pentahydrate and then standardized titrimetrically(6).

Cadimum (II) solution 1 x 10^{-2} M.: Prepared from analytical reagent grade cadmium acetate and standardized (6) gravimetrically. Solutions of lower concentration were prepared by diluting this solution as required.

All the other chemicals used were of AnalaR grade, and their solutions were prepared in doubly distilled water. A 0.002% freshly prepared gelatin was used as the maximum suppressor.

Apparatus

A Toshniwal Model CLO 2A Manual Polarograph coupled with a type MG-2 Galvanometer was used. A SCE was used as the reference. Oxygen was expelled by passing a stream of purified nitrogen through the test solution for 10 min. Doubly distilled mercury was used. The capillary characteristics of dropping mercury electrode at constant height (76.5 cm) of mercury head were as follows, t = 3.8 s; m = 2.482 mg s^{-1} in 0.1 M KNO_3 solution in open circuit. A Lingane type H-cell and a Model LI-120 ELICO pH Meter were also used. A Toshniwal type GL 15 thermostat was used to regulate the temperature at 26 ± 0.1°C.

RESULTS AND DISCUSSION

The results obtained for Cu-ST complex in 0.1 M KNO_3 supporting electrolyte medium are presented here. Polarograms were recorded at various pH values keeping other factors [such as metal ion concentration (1.0 mM), ligand concentration 0.1 M) constant. A well defined wave was obtained in the pH range 9.5 - 12.5. The diffusion current did not change in this pH range.

The Cu-ST complex in 0.1 M KNO_3 medium gave a double wave showing step-wise reduction. First to Cu (1) and them to Cu(0).

The early part of the first reduction coincides with the anodic mercury dissolution curve. The current-voltage curves of the second wave are used in further analysis. The slope of the log plot showed that the reduction is a one electron reversible process.

The slope values are given in Table 1. The plots of $-E_{1/2}$ as a function of sucessive complexes and hence DeFord and Hume's method was employed for determining various complexity functions, $F_j[X]$. $F_2[X]$ vs C_x shows a horizontal line parallel to

TABLE 1

DERIVED FUNCTIONS OF COPPER-ST SYSTEMS
[Cu(II)] = 0.2 mM, [KNO_3] = 0.1 M,
pH = 10.5, Gelatin = 0.002%

[ST]	id	Slope	$E_{1/2}$ (-V vs SCE)		$\Delta E_{1/2}$ (-V vs SCE)
(M)	(μA)	(mV)	Cu(II)	Cd(II)	
0.00	1.52	59.0	0.210	0.590	0.000
0.02	1.40	61.4	0.401	0.728	0.191
0.03	1.35	60.2	0.403	0.729	0.193
0.04	1.29	59.1	0.404	0.730	0.194
0.05	1.27	59.3	0.408	0.732	0.198
0.06	1.25	59.1	0.416	0.734	0.206
0.08	1.22	59.1	0.424	0.742	0.214
0.10	1.14	59.0	0.431	0.745	0.221
0.20	1.00	59.1	0.446	0.758	0.236
0.40	0.99	59.1	0.463	0.768	0.253
0.60	0.76	59.0	0.469	0.776	0.259
0.80	0.72	59.0	0.476	0.780	0.266
1.00	0.68	59.0	0.481	0.782	0.271

C_x axis (Fig. 1) indicating that the highest complex formed is 1:2. The plots of $F_1[X]$ and $F_2[X]$ vs ligand (ST) concentrations when extrapolated to $C_x = 0$ gave values for the stepwise formation constants for Cu-ST complexes. Moreover, the slope values of $F_0[X]$ and $F_1[X]$ curves coincide with the intercept values of $F_1[X]$ curves respectively. The stability constants of Cu-ST complexes are $\beta_1 = 7.5 \times 10^7$ and $\beta_2 = 8.0 \times 10^9$ and these are compared with the previously reported (7) values of Cd-ST complex ($\beta_1 = 1.1 \times 10^7$ and $\beta_2 = 8.0 \times 10^9$). The order of stability constants of these complexes can be represented as

β_1 (Cu - ST) > β_1 (Cd - ST)

β_2 (Cu - ST) > β_2 (Cd - ST)

The stability constant sequence follows the order of second ionization potential of copper (20.3) and cadimum (16.8).

DETERMINATION OF Cu(II) AND Cd(II)

Calibration graphs were constructed for the copper ion concentration (0.5 - 1.6 mM) and cadmium (0.5 - 1.8 mM) ion concentration versus diffusion current in 0.1 M ST, with 0.1 M KNO_3 supporting electrolyte medium.

From the individual polarograms of copper and cadmium, it was possible to differentiate the two metal ions in ST solution because their half-wave potentials differed by more than 0.3 V (cf. Table 1). Consequently a series of polarograms were recorded with individual metal solutions and

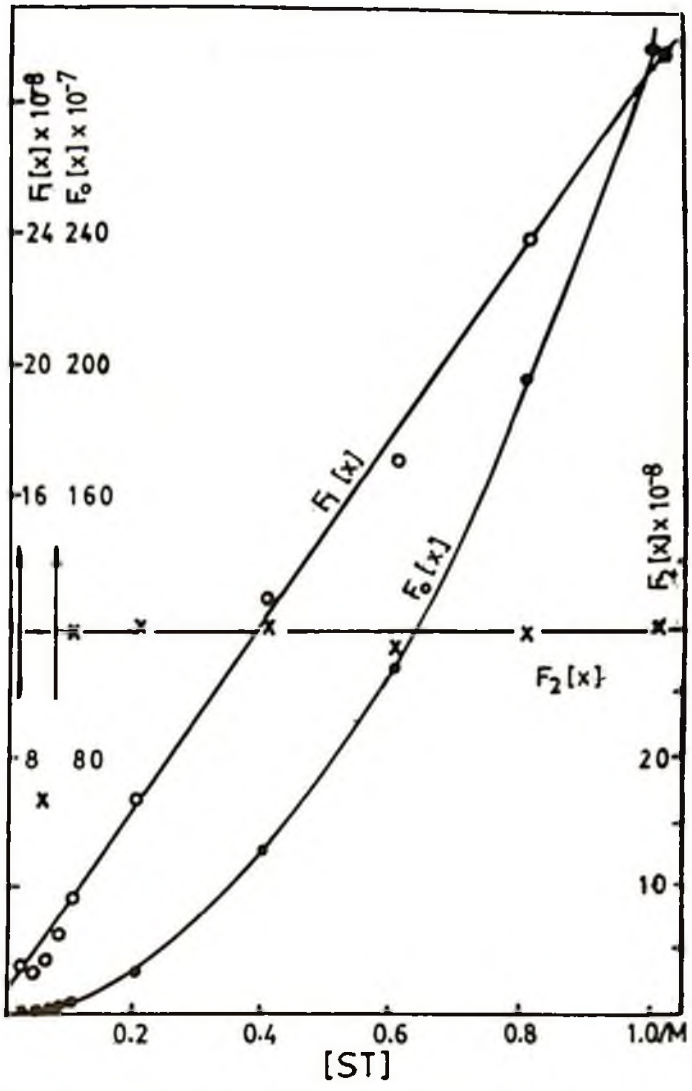


Fig. 1 Derived Functions for Cu-ST System.

synthetically mixed solutions of cations and id values referred to the respective calibration graph. The results obtained in the simultaneous determination of these metal ions are given in Table 2.

The method was extended to the analysis of aeral alloy. A sample containing a 1.5 g of the alloy was dissolved in concentrated hydrochloric acid in the presence of a few drops of nitric acid. The solution was heated until the volume had been reduced to about 2 ml and then cooled. 5 ml of dilute hydrochloric acid were added and the volume was made upto 100 ml in a calibrated flask with distilled water. An aliquot of this solution was taken and metal ions (Cu and Cd) were simultaneously determined as described above. The results are included in Table 2.

TOLERANCE LIMIT OF FOREIGN IONS

The tolerance limit of various anions and metal ions at a fixed concentration of copper and

TABLE 2

DETERMINATION OF METAL IONS WITH ST AS A COMPLEXING AGENT
[ST] = 0.1 M, pH = 10.5 and Sensitivity = 0.05

Simple No.	Amount of metal ion taken/mg		Amount of metal ion found/mg		Error %	
	Cu	Cd	Cu	Cd	Cu	Cd
1	0.397	1.380	0.395	1.378	-0.51	-0.18
2	0.794	2.760	0.799	2.752	+0.39	-0.29
3	1.598	3,312	1.604	3.332	+0.04	+0.60
4	2.223	4.416	2.210	4.426	-0.60	+0.25
5	2.542	-	2.523	-	-0.72	-
1*	0.508	2.810	0.508	2.784	-	-0.92
2*	0.763	2.248	0.762	2.248	-	-
3*	1.017	1.124	1.008	1.124	-0.81	-
4*	1.589	0.562	1.569	0.562	-1.21	-
1#	1.192	0.521	1.182	0.523	-0.83	+0.40
2#	1.738	0.786	1.746	0.779	+0.47	-0.87

Note: * Simultaneous Determination of Copper and Cadmium in a mixture

\# Simultaneous Determination in an aeral alloy of composition:
Cu 4.5%, Mg 1.2%,
Mn 0.25% and Cd 2.0%

cadmium (1.0 mM) were determined. In the presence of nitrate, acetate, sulphate and oxalate, the $E_{1/2}$ values remained almost constant in all instances. Among the metal ions examined only Pb(II), Sb(III) and In(III) interfered in the determination of copper or cadmium. Tl(I), Zn(II), Mn(II), Fe(II), and V(V) did not interfere when they are present upto a 5-fold excess. Alkaline earth metal ions Cd(II) Ba(II), Mg(II) and Sr(II) did not interfere in either determination upto a 25-fold excess.

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