THE EFFECT OF SUPPORTING ELECTROLYTE ON THE STABILITY CONSTANT OF Cd-SCHIFF BASE COMPLEX

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Synthesis of salicylaldehyde tris(hydroxymethyl)methylamine [1] (ST), and its complexation behaviour have been reported [1-2]. In the present work we have quantitatively examined the composition and stability constant of Cd-ST complex using polarographic technique giving special attention to the effect of supporting electrolytes on the stability constant of this schiff base complex.

EXPERIMENTAL

Manual Toshniwal polarographic model CLO 2A coupled with Galvonometer type MG-2 was used to record the polarograms. The capillery characteristics of dme at constant height of mercury head (h = 76.5 cm) were t = 3.8 sec; m = 2.482 mg/sec at 0 V vs SCE in water. A Lingane type H-cell and a digital pH meter (Model LI-120, ELICO) were used in the present study. A Toshniwal thermostat type GL-15 was used to keep the temperature at 26 ± 0.1°C.

A stock solution (0.1 M) of cadmium(II) was prepared using AR cadmium acetate and standardized gravimetrically [3]. ST was prepared by following the literature procedure [1] and reagent solution (2.0 M) was prepared in 60% aqueous dimethylformamide.

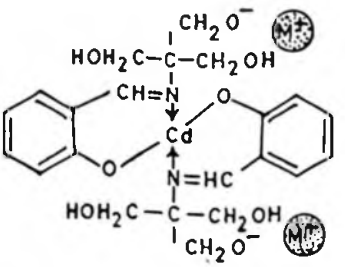
All reagents used were of AnalaR (BDH) grade and their solutions were prepared in doubly distilled water. All polarographic experiments were done in 30% aqueous dimethylformamide medium. A 0.002% freshly prepared gelatin was used as maximum suppressor.

RESULTS AND DISCUSSION

The results obtained for Cd-ST complex in different supporting electrolytes (0.1 M KCl, Li_2SO_4, $NaClO_4$) in pH range 7-12 are presented here. Well defined polarograms were obtained in the pH range 9.0 - 12.0. Hence pH 10.5 was selected for further studies. Cathodic reduction of Cd(II) was found to be reversible in the presence of ST in all supporting electrolytes employed as revealed by the straight line plots of E_{de} vs log $[i/(i_d - i)]$. The diffusion controlled nature of reduction was confirmed by proportionality of diffusion current to the square root of effective height of mercury column and to the concentration of cadmium in each supporting electrolyte studied.

With increase in the concentration (0.02 - 1.0 M) of ligand (ST), the half-wave potential shifted towards more negative value and diffusion current is decreased. The log plots were found to be linear with slope values in good agreement with two electron reduction. (Table 1). The plots of $-E_{1/2}$ as a function of -log [X] for Cd-ST system in all supporting electrolytes employed shows the formation of successive complexes and hence DeFord and Hume's method [4] was employed for determining various complexity functions, $F_j[X]$. $F_2[X]$ vs C_x shows a horizontal line parallel to the C_x axis which indicates the maximum complex in this medium is of formula 1:2. The plots of $F_1[X]$ and $F_2[X]$ vs ligand (ST) were used to determine the stepwise formation constants of cadmium complex in every supporting electrolyte of present study. The stability constant data of complex are presented in Table 2.

In alkaline medium, the deprotanation of phenolic hydroxyl group and bond formation between metal ion and oxygen [5-7] is expected besides the coordination of azomethine nitrogen atom [7,8] to cadmium. Since cadmium is known to form 4-coordinate complexes, the following structure for Cd-ST complex is suggested.



The structure of Cd-St complex and its interaction with alkali metal ions of supporting electrolyte

Based on overall stability constant (β_2) data (Table 2) the order of stability of cadmium-ST complex in three different electrolytes is represented as

$$KCl > Li_2SO_4 > NaClO_4 \qquad ...(1)$$

The influence of nature of supporting electrolyte on the stability constants of complex has been attributed [9-12] to various factors such as inter-ionic forces, conductanoe, viscocity,

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TABLE 1

DERIVED FUNCTIONS FOR Cd-ST SYSTEM
[Cd] = 1.0 mM; Supporting Electrolyte = 0.1 M; pH = 10.5; Gelatin = 0.002%

[Ligand] M	i_d (μA)	Slope (mV)	$E_{1/2}$ -V. Vs. S.C.E.	$\Delta E_{1/2}$ -V. Vs. S.C.E.	Log I_M/I_C	F_o[Ligand] x 10^{-4}	F_1[Ligand] x 10^{-6}	F_2[Ligand] x 10^{-6}
KCl medium								
0.00	6.2285	29.41	0.600	0.000	0.0000	0.0001		-
0.02	6.2145	31.46	0.740	0.140	0.0010	5.2480	2.6239	-
0.03	6.2025	31.82	0.741	0.141	0.0018	5.6720	1.8906	-
0.04	6.1900	31.72	0.742	0.142	0.0027	6.1480	1.5369	-
0.05	5.9045	31.68	0.744	0.144	0.0232	7.5370	1.5074	15.1480
0.06	5.8340	30.96	0.747	0.147	0.0280	9.6160	1.6027	14.2116
0.08	5.4610	30.48	0.752	0.152	0.0572	15.1500	1.8937	14.2116
0.10	5.3320	30.81	0.756	0.156	0.0675	21.1700	2.1169	13.6690
0.20	5.0880	30.98	0.771	0.171	0.0879	70.9400	3.5469	13.9845
0.40	3.8090	30.48	0.782	0.182	0.2136	223.1000	5.5774	12.0685
0.60	3.4280	30.14	0.791	0.191	0.2594	497.1000	8.2849	12.5581
0.80	2.7740	29.96	0.796	0.196	0.3483	902.2000	11.2774	13.1592
1.00	2.0950	29.94	0.798	0.198	0.4731	1403.0000	14.0299	13.2799
Li_2SO_4 medium								
0.00	6.2295	29.82	0.594	0.000	0.0000	0.0001	-	-
0.02	6.1885	32.46	0.708	0.114	0.0029	0.6997	0.3499	-
0.03	6.1245	32.02	0.710	0.116	0.0073	0.8266	0.2755	-
0.04	6.0960	31.98	0.711	0.117	0.0095	0.8984	0.2246	3.1150
0.05	5.9585	31.96	0.713	0.119	0.0193	1.0730	0.2146	2.2920
0.06	5.9016	30.85	0.716	0.122	0.0235	1.3670	0.2278	2.1300
0.08	5.8420	30.92	0.722	0.128	0.0280	2.1980	0.2747	2.1837
0.10	5.5880	30.86	0.726	0.132	0.0473	3.1350	0.3135	2.1350
0.20	5.2070	30.64	0.741	0.147	0.0779	10.7800	0.5389	2.1945
0.40	3.9370	30.84	0.752	0.158	0.1993	33.5200	0.8379	1.8448
0.60	3.3020	29.96	0.761	0.167	0.2757	80.1100	1.3352	2.0587
0.80	2.6670	29.64	0.765	0.171	0.3685	135.4000	1.6925	1.9906
1.00	2.1590	29.72	0.768	0.174	0.4603	211.0000	2.1099	2.0099
$NaClO_4$ medium								
0.00	6.2445	29.24	0.586	0.000	0.0000	0.0100	-	-
0.02	6.2350	30.64	0.658	0.072	0.0007	2.6770	1.3335	-
0.03	6.1840	30.92	0.659	0.073	0.0042	2.9120	0.9673	-
0.04	5.9470	30.74	0.660	0.074	0.0212	3.2750	0.8162	0.7905
0.05	5.8560	30.82	0.662	0.076	0.0279	3.8900	0.7760	0.5520
0.06	5.7930	30.68	0.668	0.082	0.0326	6.2610	1.0418	0.9030
0.08	5.7280	30.46	0.684	0.098	0.0375	21.9100	2.7375	2.7968
0.10	5.5380	30.21	0.691	0.105	0.0522	39.0100	3.9000	3.4000
0.20	5.2190	30.04	0.706	0.120	0.0779	132.4000	6.6195	3.0598
0.40	4.0720	29.94	0.716	0.130	0.1856	368.6000	9.2147	2.1787
0.60	3.4370	29.86	0.725	0.139	0.2594	879.8000	14.6631	2.3605
0.80	2.5460	29.72	0.729	0.143	0.3897	1537.0000	19.2123	2.3390
1.00	2.0360	29.68	0.733	0.147	0.4866	2765.0000	27.6499	2.7149

over-voltage and adsorption. So no generalization is made. The variation in the stability constants of Cd-ST complex in different media may be due to the difference in the extent of hydration of cations of supporting electrolyte

The hydration number is the measure of extent of hydration, which was defined [20] as

$$H = [A - (\gamma_+ + \gamma_-)] \quad \ldots (2)$$

TABLE 2

STABILITY CONSTANTS OF CADMIUM-ST COMPLEX IN DIFFERENT SUPPORTING ELECTROLYTES

Supporting Electrolyte	Stability constant	
	β_1	β_2
KCl	7.5×10^5	13.0×10^6
KNO_3	1.1×10^6	8.0×10^6
Li_2SO_4	1.0×10^5	2.0×10^6
$NaClO_4$	5.0×10^3	2.4×10^5

where γ_+ and γ_- represent the crystallographic radii of the cation and anion of the electrolyte used. 'A' represents the sum of the crystallographic radii of the cation and anion of electrolyte when hydration is zero. This point has been discussed in detail by Robinson and Strokes [21]. The extent of hydration appears to be in the following order.

$$K^+ < Li^+ < Na^+ \quad \ldots (3)$$

The high stability constant of Cd-ST complex in KCl medium is attributed to the ability of K^+ ions to nullify the ionic character of hydroxo groups, which thereby minimizes its electron withdrawing effect, facilitated by less shielding of K^+ ions due to hydration. The low stability constant of Cd-ST complex in $NaClO_4$ medium may be due to the high shielding effect due to hydration of Na^+ ions. These ions may not be successful in decreasing the ionic character of hydroxo groups.

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