Polarographic Behaviour of {3-Hydroxy-3-*o*-Tolyl-1-(*p*-Carboxyphenyl) Triazene} (HOTCPT) ion and {3-Hydroxy-3-Ethyl-1-(*p*-Carboxyphenyl) Triazene} (HECPT) Ion with Cadmium

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The overall formation constants of the hydroxy triazene complexes were determined polarographically by DeFord and Hume's method as modified by Irving. These compounds have been synthesized for the first time. The percentage distribution of cadmium present in various forms as a function of ligand concentration was also calculated

INTRODUCTION

Hydroxytriazenes are well known groups of chelating agents. Their applications as spectrophotometric reagents as well as metallochromic indicators for the complexometric determination of a number of transition metal ions are well established. A survey of literature reveals that till 1992 several reviews[1–3] have appeared on hydroxytriazenes.

Hydroxytriazenes, in general, are prepared by two methods. Bamberger[4] and Gebhard and Thompson[5] have described their preparation by reducing nitro or nitroso-benzene with phenyl hydrazine or substituted phenyl hydrazine. The second method consists in reacting diazonium salt or substituted diazonium salt with phenyl or alkyl hydroxylamine in acetate buffered solution at 0° to 3°C. During the present investigations we have adopted the second method and studied the formation constants polarographically with cadmium metal.

EXPERIMENTAL

All the chemicals used were of reagent grade. The solution of cadmium was prepared from cadmium nitrate in distilled water and standardised by conventional method. In each case concentration of Cd^{2+} was 1 mM. The ionic strength was kept constant at 0.5 M by adding $NaClO_4$. A 0.002% Triton-X-100 was used as maxima suppression. The sodium salts of {3-hydroxy-3-*o*-tolyl-1-(*p*-carboxyphenyl) triazene} (HOTCPT) and {3-hydroxy-3-ethyl-1-(*p*-carboxyphenyl) triazene} (HECPT) were used. The polarograms were recorded using manually operated polarographs. The dropping mercury electrode had the following characteristics: $m = 3.50$ mg S^{-1} and $t = 3.1$ sec (open circuit). An H-type cell saturated with sodium chloride agar-agar bridge was used. The temperature was kept at 30 ± 0.1°C with the help of a Haake-Ultra thermostat. All the polarograms were recorded after deaeration by purging purified nitrogen gas.

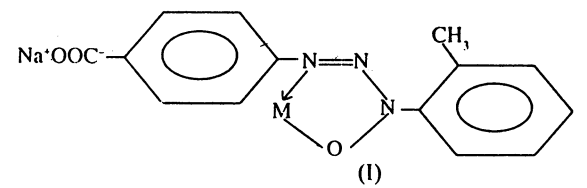
RESULTS AND DISCUSSION

In each a single well defined reduction wave appeared. The half wave potential was found to be shifted towards more negative value and the diffusion current decreased with the increase of the concentration of the ligand (HOTCPT and HECPT) ions. The plots of $\log \frac{i}{i_d - i}$ *vs.* $E_{d.e.}$ were found to be linear with the slopes of the order 29 ± 2 mV in case of cadmium-HOTCPT and 32 ± 1 mV in case of cadmium-HECPT systems indicating reversible reduction. The value of n being two, the plot of $E_{1/2}$ *vs.* log C_x was found to be a smooth curve in each case showing the formation of two or more complex species in equilibrium. The classified method of DeFord and Hume[6] as modified by Irving[7] was applied. The overall formation constants were calculated by the graphical extrapolation of $F_j([X])$ functions to the zero ligand concentration. The values of $F_j([X])$ calculated by this method are given in Table-1 for Cd-HOTCPT system. In case of cadmium-HOTCPT system, the plot of $F_0([X])$ *vs.* C_x was found to be a smooth curve. The $F_1([X])$ *vs.* C_x plot is a straight line. Plot of $F_2([X])$ *vs.* C_x is also a straight line and the plot of $F_3([X])$ *vs.* C_x is a straight line parallel to C_x axis which shows the presence of the last complex species.

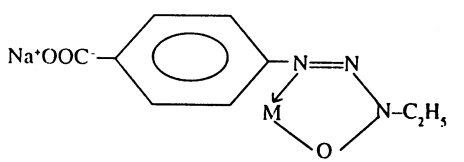
The results show the presene of three complex species $Cd([X])^+$, $Cd([X])_2$ and $Cd([X])_3^-$ where [X] represents HOTCPT ions.

In case of cadmium-HECPT system, the plots of $F_0[X]$ and $F_1[X]$ *vs.* C_x were smooth, $F_2([X])$ *vs.* C_x a straight line with some slope and $F_3([X])$ *vs.* C_x a straight line parallel to the C_x-axis. These results show the presence of three complex species having composition $[Cd(Y)]^+$, $[Cd(Y)_2]$ and $[Cd(Y)_3]^-$ where (Y) represents the HECPT ions.

The results are given in Tables 1–4 and figures 1(a) to 2(c). This is cleared from these tables that the complexes formed by HECPT ions are more stable than those formed by HOTCPT ions.



(I)



(II)

TABLE-1

POLAROGRAPHIC CHARACTERISTICS AND ANALYSIS OF $F_j([X])$ FUNCTIONS OF CADMIUM-HOTCPT SYSTEM AT 30°C ($\mu = 0.5$)

$\beta_1 = 36 \times 10^{14}$, $\beta_2 = 39 \times 10^{14}$, $\beta_3 = 125 \times 10^{14}$

C_x (moles)	$E_{1/2}$ (–V*vs*.S.C.E.)	i_d (divis.)	$F_0([X])$ $\times 10^{-13}$	$F_1([X])$ $\times 10^{-14}$	$F_2([X])$ $\times 10^{-14}$	$F_3([X])$ $\times 10^{-14}$
0.00	0.5810	47.5	–	–	–	–
0.05	0.5900	40.5	4.320	36.21	–	–
0.10	0.5915	38.5	5.115	41.15	51.5	125
0.15	0.6035	36.0	7.688	44.595	57.3	122
0.20	0.6040	35.0	10.688	48.44	62.2	116
0.25	0.6100	35.4	14.187	52.75	67.0	112
0.30	0.6135	34.0	18.577	58.59	75.3	121
0.40	0.6160	33.0	29.640	71.60	89.0	125
0.45	0.6200	33.0	36.660	79.26	96.15	127

Cd^{2+}-HOTCPT System at 30°C

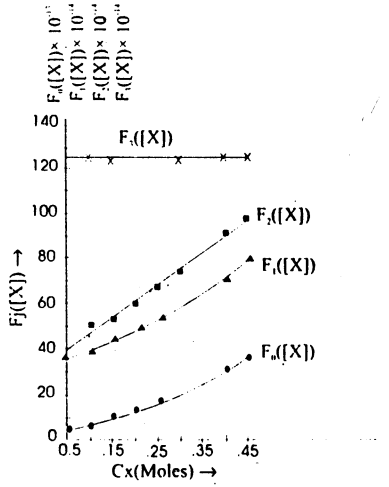


Fig.1a. Plots of Fj([X]) Vs Cx at 30°C

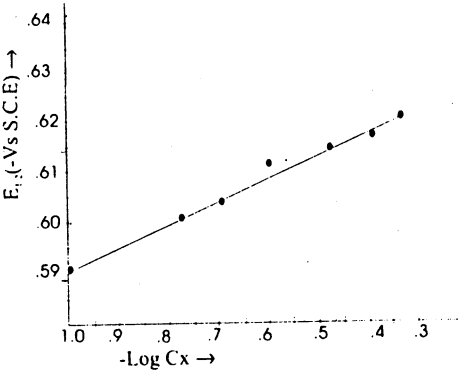


Fig.1b. Plots of $E_{1/2}$ Vs -Log Cx

TABLE-2
RELATIVE DISTRIBUTION OF Cd(II) SIMPLE AND COMPLEX WITH 3-HYDROXY-3-*o*-TOLYL-1 (*p*-CARBOXY PHENYL) TRIAZENE

Total Cd(II) Ion Concentration = 0.5 mM

C_x	M^{2+}	Mx^{2+}	Mx_2^{2+}
0.05	35.346	54.278	4.278
0.10	18.565	60.759	12.648
0.15	11.552	60.848	20.278
0.20	7.672	58.692	26.848
0.25	5.310	55.158	32.078
0.30	5.110	49.788	35.138
0.35	4.756	54.098	45.038
0.40	4.026	43.268	41.428
0.45	3.523	40.416	39.023

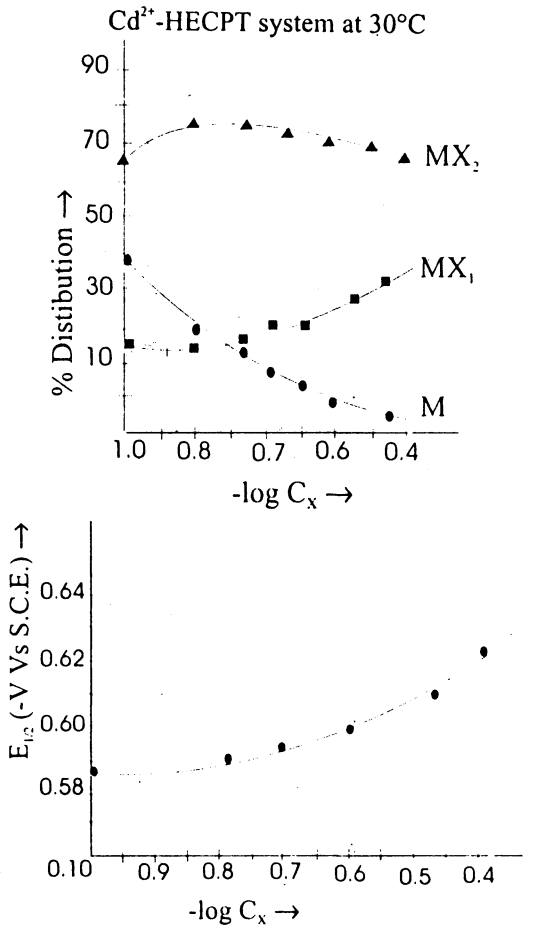


Fig.2(a). Plots of $E_{1/2}$ Vs -Log C_x

TABLE-3
POLAROGRAPHIC CHARACTERISTICS AND ANALYSIS OF $F_j([X])$ FUNCTIONS OF CADMIUM-HECPT SYSTEM AT 30°C ($\mu = 0.5$).

$\beta_1 = 39 \times 10^{13}$, $\beta_2 = 47 \times 10^{14}$, $\beta_3 = 165 \times 10^{14}$

C_x (moles)	$E_{1/2}$ (–V *vs.* S.C.E.)	i_d (divis.)	$F_0([X]) \times 10^{-13}$	$F_1([X]) \times 10^{-14}$	$F_2([X]) \times 10^{-14}$	$F_3([X]) \times 10^{-14}$
0.00	0.5710	60.00	–	–	–	–
0.05	0.5810	52.00	3.095	41.90	58.00	–
0.10	0.5833	51.00	5.539	45.39	63.90	169
0.15	0.5905	50.00	8.471	49.80	72.05	167
0.20	0.5930	47.00	12.040	55.20	81.02	170
0.25	0.6005	46.75	16.270	61.06	88.25	165
0.30	0.6006	45.25	21.360	67.86	96.21	164
0.35	0.6100	44.25	27.280	75.10	103.14	160
0.40	0.6115	42.25	34.680	84.21	113.03	165
0.45	0.6125	41.00	43.100	93.56	121.25	165

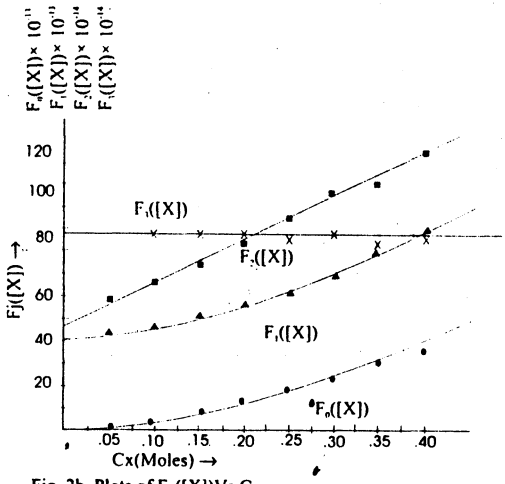


Fig. 2b. Plots of F_j ([X])Vs Cx

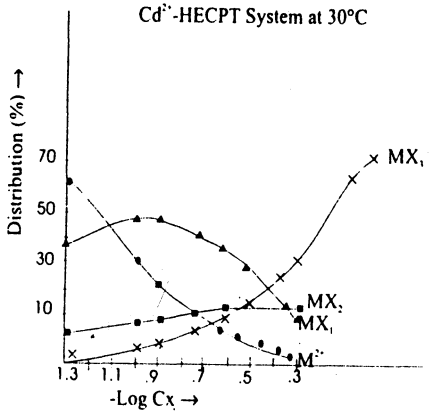


Fig 2(c)% Composition of Various Species Vs -Log Cx

TABLE-4
RELATIVE DISTRIBUTION OF Cd(II) SIMPLE AND COMPLEX WITH 3-HYDROXY-3-ETHYL-1-(*p*-CARBOXY PHENYL) TRIAZENE

C_x	M^{2+}	M_x^+	Mx_2
0.05	21.32	51.36	45.63
0.10	11.64	46.75	42.34
0.15	7.00	43.78	35.72
0.20	5.12	35.13	56.96
0.25	3.23	32.26	63.20
0.30	2.31	28.44	68.77
0.35	1.88	25.16	74.89
0.40	1.59	21.20	77.23
0.45	1.32	19.66	80.11

The structure (II) reveals that the ethyl group position '3' in ligand has a pronounced +I effect and thus perhaps gives larger stability to the complexes while in ligand (I), the *o*-tolyl group in position '3' has – I effect and thus forms less stable complexes.

The values of overall formation constant for Cd-HOTCPT systems are $\beta_1 = 36 \times 10^{14}$, $\beta_2 = 39 \times 10^{14}$, and $\beta_3 = 125 \times 10^{14}$ and in Cd-HECPT systems are $\beta_1 = 39 \times 10^{13}$, $\beta_2 = 47 \times 10^{14}$, and $\beta_3 = 165 \times 10^{14}$

The percentage distribution of cadmium present in various forms as a function of logarithum of ligand concentration was calculated by the following equations:

$$\frac{1}{F_0([X])} = \frac{(M)}{C_M} \quad \text{(i)} \qquad \frac{MX_j}{C_M} = \frac{B_j MX_j}{C_M} \quad \text{(ii)}$$

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