Asian Journal of Chemistry Vol. 12, No. 3 (2000), 758–764

Determination of Kinetic Parameters and Formation Constants of In(III)-{3-Hydroxy-3-*o*-Tolyl-1-(*p*-Carboxyphenyl) Triazene} (HOTCPT) and In(III)-{3-Hydroxy-3-Ethyl-1-(*p*-Carboxyphenyl) Triazene} (HECPT) Complexes

RAJENDRA KUMAR LOHIYA, S.K. MUKHERJI and R.V. SINGH*
Department of Chemistry
University of Rajasthan, Jaipur-302 004, India.

The interaction of In^{3+} with hydroxy triazene has been studied at dropping mercury electrode at a constant ionic strength. The reductions were diffusion controlled but quasi-reversible. The $E^r_{1/2}$ have been obtained by Gelling's method and the formation constants of the complexes formed have been evaluated by Deford and Hume's method. In(iii) forms four complex species with 3-hydroxy-3-*o*-tolyl-1-(*p*-carboxyphenyl) triazene (HOTCPT) and 3-hydroxy-3-ethyl-1-(*p*-carboxyphenyl) triazene} (HECPT) ions having $\beta_1 = 5.5 \times 10^{12}$, $\beta_2 = 7.1 \times 10^{13}$, $\beta_3 = 50 \times 10^{14}$, $\beta_4 = 384 \times 10^{14}$ and $\beta_1 = 1.2 \times 10^{12}$, $\beta_2 = 4 \times 10^{13}$, $\beta_3 = 112 \times 10^{15}$, $\beta_4 = 8.8 \times 10^{18}$.respectively. The kinetic parameters have been calculated by Meites and Israel method. The value of K_s comes of the order of 10^4 cm sec^{-1} confiriming the quasi-reversible nature of the electrode process. With increase in complexing agent concentration, the value of K_s slightly decreases indicating the increase irreversibility of the electrode process.

INTRODUCTION

Due to the importance of nitrogen containing compounds in biochemical, analytical and pharmaceutical fields, such compounds are attracting wide attention in different fields of research. Jain and Gaur[1, 2] have used polarographic method to determine the formation constant of the complex formed by metal ions with complexing agents which are reversibily reduced at dropping mercury electrode. The stability constants of Pd(II), Cu(II), Ni(II), Zn(II) and Mn(II) complexes of various hydroxy triazenes using Bjerrum-Calvin pH titration technique and the stability sequence and linear co-relationship between pK_a, log β_1 and log β_2 have been reported by Purohit and co-researchers.[3] The polarographic studies on the electrode kinetics of the metal ions in some other complexing agents have also been reported by several researchers[4–11]. The present study deals with the polarographic determination of electrode kinetics of In(III) in presence of HOTCPT and HECPT ions as complexing agents in aqueous media with $NaClO_4$ as supporting electrolyte. The determination of the stability constants of the metal complexes with these ligands have been reported for the first time by polarographic method using DeFord and Hume's method.

EXPERIMENTAL

All the reagents were of AR grade. A solution of In(III)-nitrate was prepared with doubly distilled water. 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 as complexing agents. Solution of 0.35 mM of In(III) with varying concentration of the ligand used and ionic strength (1.0 μ) were maintained by addition of sodium perchlorate solution. The pH of the solution was kept 6.2 ± 0.1. For this purpose perchloric acid or sodium hydroxide were used. A manual polarographic set was used for polarographic measurements for obtaining C-V curves. The d.m.e. having the characteristics $m = 2.7$ mg/sec and $t = 2.80$ sec was used. Throughout the measurement all the experiments were carried out at 30°C, unless otherwise stated, which was maintained with Haake type ultrathermostat (±0.01°C). Triton-X-100 has been used as maximum suppressor. The polarograms have been recorded after deaeration (30–35 min) of the solution with purified nitrogen gas. H-type cell with agar-agar plug saturated with sodium chloride served as electrolytic cell.

RESULTS AND DISCUSSION

For all the solutions in each system, a single well defined diffusion controlled reduction wave appeared. The half wave potential shifted towards more negative value and it was found to decrease with increasing concentration of HOTCPT and HECPT ions indicating the procedure of complexations. The kinetics of the electrode process has been studied by Koutecky method,[12] as modified by Meites and Israel[13]. The plots of log $\frac{i}{i_d - i}$ *vs.* $E_{d.e.}$ are linear in this case. The slopes are higher than required for three electrons reversible reductions. This indicates the elctrode process to be quasi-reversible. Reversible half wave potential ($E^r_{1/2}$) has been determined by Gellinges method[14] by plotting $\left[E - \frac{RT}{nF} \ln \frac{i_d - i}{i}\right]$ *vs.* i. The standard rate constants have been calculated from the plots of log $(Z - 1)$ *vs.* $(E - E^r_{1/2})$, which result in a straight line. From the slopes and intercepts of these plots, the values of K_s and α have been calculated. The value of K_s comes to be of the order of 10^4 cm/sec which confirms that the reduction process is quasi-reversible. From the K_s values it is obvious that the electrode process becomes less irreversible in the presence of HOTCPT and HECPT ions. The plot of $E^r_{1/2}$ *vs.* log C_x was found to be a straight line. The plot of $F_0([X])$ *vs.* C_x is a smooth curve, indicating the formation of more than one complex species which are in equilibrium. The overall formation constants were obtained by De-Ford Hume's method[15] by extrapolation of $F_j([X])$ function to $C_x = 0$. Four complex species $[In(HOTCPT)]^{2+}$, $[In(HOTCPT)_2]^+$, $[In(HOTCPT)_3]$ and $[In(HOTCPT)_4]^-$ are formed and their formation constants are $\beta_1 = 5.5 \times 10^{12}$, $\beta_2 = 7.1 \times 10^{13}$, $\beta_3 = 50 \times 10^{14}$, $\beta_4 = 384 \times 10^{14}$. The value of β_4 has also been

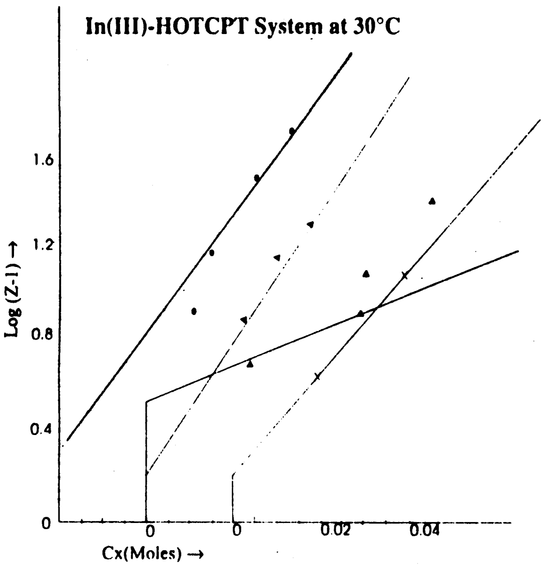


Fig. 1(a). Plots of log (Z – 1) *vs.* C_x for HOTCPT System at 30°C

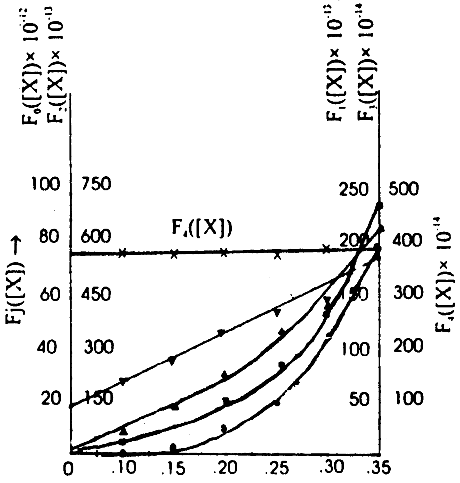


Fig. 1(b). Plots of F_j *vs.* C_x for HOTCPT System at 30°C

calculated by Lingane's[16] method. The value of β_4 comes out to be 377×10^{14} by Lingane's method.

Four complex species $[In(HECPT)]^{2+}$, $[In(HECPT)_2]^+$, $[In(HECPT)_3]$ and $[In(HECPT)_4]^-$ are forme and their formation constants are $\beta_1 = 1.2 \times 10^{13}$

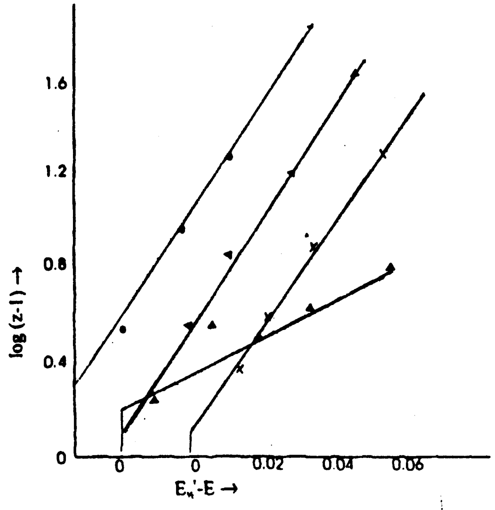


Fig. 2(a). Plots of log (Z – 1) *vs.* $E^r_{½}$-E In(III)-HECPT System at 30°C

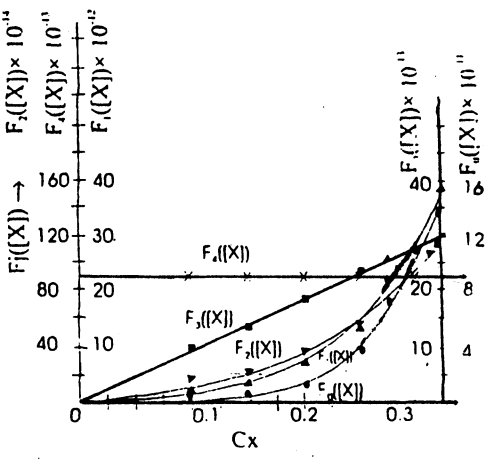


Fig. 2(b). Plots of $F_j([X])$ *vs.* C_x In(III)-HECPT System at 30°C

$\beta_2 = 14 \times 10^{13}$, $\beta_3 = 112 \times 10^{15}$ and $\beta_4 = 8.8 \times 10^{18}$. The value of β_4 comes out to be 8.29×10^{18}. A survey of the values of the stability constants of various metal-HECPT systems reveals that the order of the stabilities of the complexes is as follows:

$$In^{3+} > Eu^{3+} > Cd^{2+} > Pb^{2+}$$

It is clear that the complexes formed by In^{3+} are stronger than formed by Cd(II) and Pb(II). The results can be explained on the basis of the ionic size of the ions

TABLE-1

POLAROGRAPHIC CHARACTERISTICS, $F_j([X])$ VALUES AND KINETIC PARAMETERS FOR In(III)-HOTCPT COMPLEXES AT 30°C ($\mu = 1.0$)

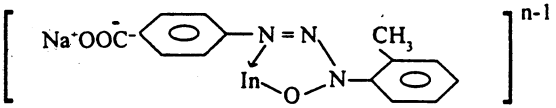
C_x (mol)	I_d (μA)	$E_{1/2}$ (–V *vs.* S.C.E.)	$E^r_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$ $\times 10^{-13}$	$F_1([X])$ $\times 10^{-13}$	$F_2([X])$ $\times 10^{-15}$	$F_3([X])$ $\times 10^{-15}$	$F_4([X])$ $\times 10^{-15}$	α	λ ($sec^{1/2}$)	$D^{1/2} \times 10^3$ (cm^2/sec)	$K_s \times 10^4$ ($cm\ sec^{-1}$)
0.00	5.43	0.5594	0.540	–	–	–	–	–	0.4717	0.3116	1.2	3.713
0.10	5.22	0.8100	0.801	2.505	15.05	95.5	88.40	384	0.6107	0.3502	1.2	4.152
0.15	5.15	0.8240	0.814	5.590	30.60	167.3	106.85	379	0.4809	0.4220	1.1	4.613
0.20	4.80	0.8400	0.824	12.480	57.40	259.5	126.20	381	0.4108	0.4290	1.1	4.821
0.25	4.81	0.8476	0.831	25.630	98.53	372.1	146.00	384	0.4435	0.4019	1.1	4.412
0.30	4.66	0.8515	0.841	47.810	156.04	501.8	164.90	383	0.4108	0.4725	1.0	4.735
0.35	4.62	0.8610	0.842	83.750	236.44	659.8	186.50	390	0.3740	0.4725	1.0	4.735

TABLE-2

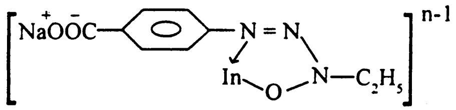
POLAROGRAPHIC CHARACTERISTICS, $F_j([X])$ VALUES AND KINETIC PARAMETERS FOR In(III)-HECPT SYSTEM ($\mu = 1.0$)

C_x (mol)	I_d (μA)	$E_{1/2}$ (–V *vs.* S.C.E.)	$E^r_{1/2}$ (–V *vs.* S.C.E.)	$F_0([X])$ $\times 10^{-13}$	$F_1([X])$ $\times 10^{-13}$	$F_2([X])$ $\times 10^{-15}$	$F_3([X])$ $\times 10^{-15}$	$F_4([X])$ $\times 10^{-15}$	α	λ ($sec^{1/2}$)	$D^{1/2} \times 10^3$ (cm^2/sec)	$K_s \times 10^4$ ($cm\ sec^{-1}$)
0.00	6.82	0.5782	0.569	–	–	–	–	–	0.5131	0.4182	1.2	3.221
0.10	6.76	0.8267	0.815	11.235	11.255	100.35	1002.1	8901	0.6509	0.4296	1.2	4.398
0.15	6.51	0.8438	0.832	50.590	33.730	216.85	1444.7	8885	0.5261	0.4311	1.1	4.761
0.20	6.12	0.8619	0.852	152.120	76.060	374.30	1870.8	8794	0.4503	0.4375	1.1	4.920
0.25	5.84	0.8724	0.863	365.275	146.110	579.64	2318.0	8824	0.4916	0.4012	1.1	4.516
0.30	5.57	0.8816	0.872	748.060	249.350	827.18	2756.8	8816	0.4511	0.4863	1.0	4.733
0.35	5.11	0.8922	0.881	1369.340	391.240	1119.40	3183.6	8776	0.4126	0.4914	1.0	4.746

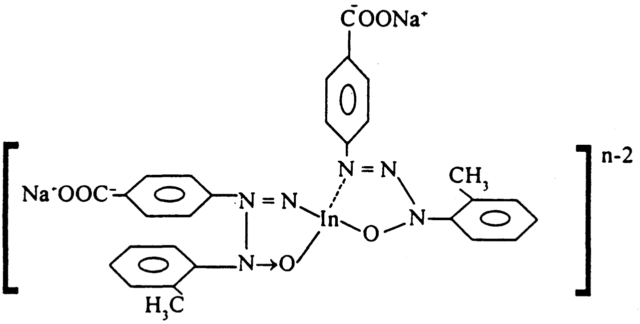
involved in complex formation. The ionic size of these ions is gradually increasing and the extent of coordination may decrease in the same order. The proposed structures may be written as:



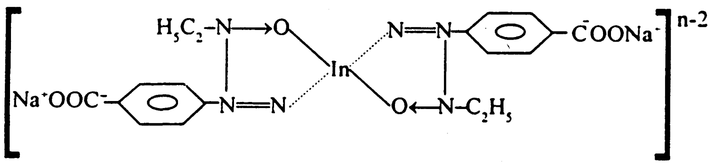
In (III) - HOTCPT (1 : 1)



In (III) - HECPT (1 : 1)



In (III) - HOTCPT (1 : 2)



In (III) - HECPT (1 : 2)

ACKNOWLEDGEMENT

One of the authors (R.K. Lohiya) is thankful to the Head of the Chemistry Department, Rajasthan University, Jaipur for providing necessary facilities for completing this piece of work.

REFERENCES

1. D.S. Jain and J.N. Gaur, *Rev. Polar. Japan*, **28,** 183 (1973).
2. ————, *J. Less Common Metals*, **60,** 179 (1978).
3. D.N. Purohit, Chyan Mehta and Rekha Bhatt, *Oriental J. Chem.*, **9,** 258 (1993).
4. D.S. Jain and K. Zutshi, *J. Electroanal. Chem.*, **5,** 389 (1963).
5. Sadhana Agarwal and D.S. Jain, *Transactions of SAEST*, **26,** 166 (1991).
6. S.N. Mukerjee and A. Chakravarthy, *J. Indian Chem. Soc.*, **39,** 149 (1962).
7. I.M. Kolthof and T.B. Reddy, *J. Electrochem. Soc.*, **108,** 980 (1961).
8. J.F. Coetzee and J.L. Hedrick, *J. Phys. Chem.*, **67,** 221 (1964).
9. Km Krishna, Km Anju Varshney, M.C. Dubey and S.K. Jha, *J. Indian Chem. Soc.*, **57,** 658 (1980).
10. S.K. Bhasin, Om Parkash, J.N. Gaur and D.S. Jain, *J. Electrochem. Soc. India*, **28,** 147 (1979).
11. R. Brdicka, *Coll. Czech. Chem. Commun.*, **2,** 489 (1930); **3,** 396 (1931).
12. J. Koutecky, *Collect. Czech. Chem. Commun.*, **18,** 597 (1953).
13. L. Meites and Y. Israel, *J. Am. Chem. Soc.*, **83,** 4903 (1961).
14. P.J. Gellings, *Z. Electro. Chem. Ber, Bunsenges*, **66,** 477 (1962).
15. D. DeFord and D.N. Humes, *J. Am. Chem. Soc.*, **73,** 5321 (1951).
16. J.J. Lingane, *Chem. Revs.*, **29,** 1 (1941).

(*Received*: 18 January 2000; *Accepted:* 10 March 2000) AJC-1993