Polarographic Study of Binary and Ternary Complexes of In(III) with γ - Picoline and Citraconic Acid

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Polarograms of In(III)- γ-Picoline-Citraconate system at pH 4.5 ± 0.02 in aqueous medium has been used to study the complexes. Deford and Hume's method has been used to study the stoichiometry and formation constants of binary complexes and Schaap and Mcmaster's method was used for the study of ternary complexes. It has been observed that $[In (CA) (\gamma\text{-Pico})]^{1+}$, $[In (CA)_2 (\gamma\text{-Pico})]^{1-}$ and $[In (CA) (\gamma\text{-Pico})_2]^{1+}$ ternary complexes are formed with formation constants log β_{11} = 4 66. log β_{21} = 6 22 and log β_{12} = 4 70 respectively.

Ever since the work of Schaap and Mcmasters an increasing number of research papers have appeared, on the use of polarographic method for the study of stoichiometry and formation constants of mixed ligand complexes. In continuation of the work in our laboratory (2-6) the present paper describes the results of polarographic study on binary and ternary complexes of In (III) with γ-Picoline and Citraconic acid.

EXPERIMENTAL

Di-Sodium salt of citraconic acid was prepared and used as a ligand. Potassium chloride (1M) was used as supporting electrolyte. Indium ion concentration in polarographic solution was 1 mM. Reagent grade chemicals and double distilled water are used throughout. Deford and Hume's method was used to study the stoichiometry and formation constants of binary complexes of In (III) with γ-Picoline and Citraconate ligands separately.

For the study of ternary complexes of In (III) with these ligands Schaap and Mcmaster's method was applied.

A.C.I.C. (India) polarograph was used to record the current-voltage cueves. The capillary used had $m^{2/3}\ t^{1/6}$ = 2.316 $mg^{2/3}\ sec^{-1/2}$ in 1 M potassium chloride at 45 cm effective height of mercury column. The pH of the test solutions was adjusted to pH 4.5 ± 0.02 using dil HCl/NaOH solution. An Elico digital pH meter model LI-120 was used to read the pH of the test solutions. Purified nitrogen gas was passed through the solutions before recording polarograms. All the observations were made at 27.5 ± 0.1°C.

RESULTS AND DISCUSSION

In (III) gave a three electron, reversible, and diffusion controlled reduction wave in all the media studied. The slopes of linear plots of $\log \frac{i}{id-i}$ Vs E were of the order of 21 + 1 mV

TABLE 1

In (III) - γ Picoline System, Values of $F_i[X]$ Funtions
In (III) = 1 mM; μ = 0.1 [KCl], pH = 6.5 ± 0.02, Temp. = 27.5 ± 0.1°C.

All potentials are w.r to SCE

	[γ - Picoline]	-E 1/2 mv	id (div.)	$F_0[X]$	$F_1[X]$ X 10^{-1}	$F_2[X]$ X 10^{-3}	$F_3[X]$ X 10^{-5}
1	0.00	610	64	-	-	-	-
2	0.01	618	62	2.636	16.36	-	-
3	0.02	624	58	5.685	23.42	4.21	-
4	0.03	634	57	18.97	59.90	14.96	4.6
5	0.04	640	56	38.36	93.40	19.60	4.6
6	0.05	646	53	81.79	161.58	29.31	5.6
7	0.06	650	52	133.2	220.30	34.22	5.5

log β_1 = 2.17 log β_2 = 3.00 log β_3 = 5.54

and the plots of i_d vs h_{corr} were linear passing through origin.

BINARY COMPLEXES

Deford and Hume's treatment of the observed polarographic data was used to study the binary complexes. Table 1 and 2 represent the $F_i(X)$ functions and other relevant data for the In(III)- γ-Picoline and In(III)- Citraconate systems. The data in the table reveal the formation of three binary complexes of In(III) with each of the two ligands.

TERNARY COMPLEXES

For the polarographic studies on the ternary In-Citraconate- γ-Picoline system, two concentration of γ-Picoline were so chosen that in predaminently exists as 1:1 and I:2 complexes respectively. The concentration of citraconate was varied from 0.0 M and 0.1 M and that of γ-Picoline fixed at 0.1 M and 0.2 M respectively. A more electronegative shift in the $E_{1/2}$ values as compared to shift observed in absence of citraconate ion, was observed. This indicated the formation of ternary complexes. Schaap and Mcmaster's treatment has been used. The F_{ij} functions and A, B, C constants have been tabulated (Table 3). T sults revealed the formation of three mixed plexes viz. $[In-(CA)-(\gamma\ Pico)]^{+1}$, $[In-(CA)_2(\gamma P$ and $[In-(CA)-(\gamma-Pico)_2]^{+1}$ with for constants log β_{11} = 4.66, log β_{21} = 6.22 and l = 4.70 respectively.

The mixing constant K_M and stabilisation cor for the reaction:

$$1/2\ [In(\gamma\text{-Pico})_2] + 1/2\ [In(CA)_2] = [In(CA)(\gamma\ Pico)]^{1+}$$

(Which is a measure of relative stability o ternary complexes in solution as compared to parent binary complexes) have been calculate by the relation $K_M = \beta_{11}/\sqrt{\beta_{02} \cdot \beta_{20}}$ and log K_S K_M - log 2, respectively. The values of log 1.3133 and that of log K_S = 1.0123 show that ternary complexes are little more stable tha binary complexes. A scheme showing the ten of a ligand to add to a complex and to subst another ligand is given below:

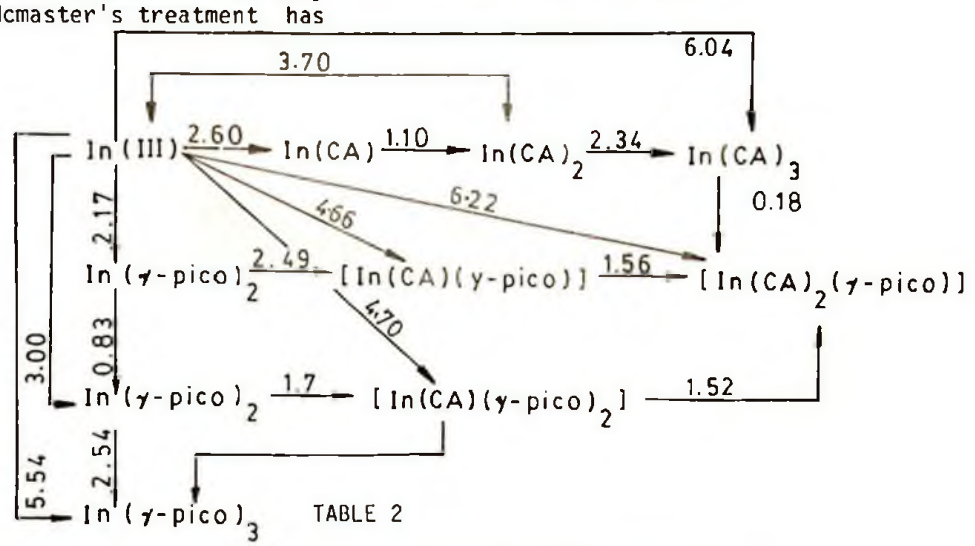


TABLE 2

In (III) - Citraconate system; Values of $F_j[X]$ Functions
In (III) = 1 mM, μ = 0.1 [KCl], pH = 6.5 ± 0.02, Temp. = 27.5 ± 0.1°C
All Potentials are withe respect to SCE.

Sl.No.	[Citraconite]	- $E_{1/2}$ mv	i_d (div.)	$F_0[X]$	$F_1[X]$ X 10^{-1}	$F_2[X]$ X 10^{-3}	$F_3[X]$ X
1	0.00	610	64	-	-	-	-
2	0.01	624	60	5.495	44.9	4.95	-
3	0.02	630	59	23.45	112.2	36.12	15.56
4	0.03	638	56	31.70	102.3	20.77	-
5	0.04	652	56	156.3	388.2	87.06	20.51
6	0.05	654	50	223.9	445.8	81.16	15.23
7	0.06	660	47	475.3	790.5	125.08	20.01

log β_1 = 2.60 log β_2 = 3.70 log β_3 = 6.04

TABLE 3

POLATROGRAPHIC CHARACTERISTICS AND F_{ij} FUNCTIONS OF

In (III) - Citraconate- γ-Picoline mixed system
In (III) = 1 mM, μ = 0.1 [KCl], pH = 6.5 ± 0.02, Temp. = 27.5 ± 0.1°C
$(E^{1/2})_S$ = 0.610 V Vs SCE; i_d (in div.) = 64 γ-Picoline = 0.1 M (fixed)

Sl. No.	Concentration of citraconate	- E 1/2 V Vs SCE	id (div.)	$F_{00}[X,Y]$	$F_{10}[X,Y]$ X 10^{-2}	$F_{20}[X,Y]$ X 10^{-4}	$F_{30}[X,Y]$ X 10^{-6}
	γ Picoline 0.1m (fixed)						
1	0.01	- 0.630	58	11.48	1.48	-	-
2	0.02	- 0.638	57	29.81	9.90	-	-
3	0.03	- 0.654	55	201.1	63.70	4.56	-
4	0.04	- 0.664	52	686.3	169.07	29.75	3.18
5	0.05	- 0.670	50	1141	226.20	35.24	3.64
6	0.06	- 0.672	48	1897	314.50	44.08	4.51
	γ Picoline 0.2m (fixed)						
7	0.01	- 0.634	56	19.05	-	-	-
8	0.02	- 0.640	56	38.02	9.01	-	-
9	0.03	- 0.654	55	199.5	59.83	-	-
10	0.04	- 0.668	52	1096	269.00	52.25	8.56
11	0.05	- 0.672	50	1821	360.20	60.04	8.40
12	0.06	- 0.676	48	3029	501.50	73.58	9.26

A = 10; B = 5000; C = 1700.00; D = 28000,0(
A' = 20; B'= 6000; C' = 1800.00; D' = 80000,0(

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