TABLE 2

DATA AND DERIVED [X] FUNCTIONS OF Zn(II)-NICOTINATE-γ-PICOLINE MIXED SYSTEM

Zn(II) = 1.0 mM, μ = 0.1 [KCl], pH = 6.6±0.02, Temp. 25±0.5°C $-(E_{1/2})_S$ = 1.10 V vs SCE i_d = 48

Nicotinate (mM)	$-E_{1/2}$	i_d (div.)	F_{00} [XY]	F_{10} [XY]	F_{20} [XY] x10^2	F_{30} [XY] x10^5
[γ Picoline] = 0.1 M fixed						
10	1.122	43	6.218	-	-	-
20	1.140	42	25.95	897	-	-
30	1.150	38	62.61	182	273	3.76
40	1.154	35	92.87	2121	280	3.00
50	1.160	35	148.4	2808	361	4.03
A = 8	B = 1000		C = 16000		D = 340000	
[γ Picoline] = 0.2 Fixed						
10	1.124	42	7.442	-	-	-
20	1.142	42	30.34	767	-	-
30	1.154	35	92.87	2595	398	6.6
40	1.160	35	148.4	3325	481	7.0
50	1.164	33	215.1	4000	520	6.4
A' = 15	B' = 1400		C' = 20000		D' = 650000	

constant [log K_M = log β_{11} - log β_{02} - log β_{20} = 0.5396] and stabilization constant [log K_S = Log K_M = 02386) are both positive and log K_S = log K_m - log 2 = 0.2386 are both positive and indicate mixed complexation is preferred.

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POLAROGRAPHY OF Zn(II)-CITRACONATE-NICOTINATE COMPLEXES

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In recent years special attention paid to the study of mixed complexation of a large number of transition and rare earth metals [1,2]. The present paper deals with the polarographic study of stoichiometry and formation constants of mixed complexes of Zn (II) with citraconic acid and nicotinic acid.

EXPERIMENTAL

The reagents used were of AnalaR/BDH grade. Experimental solutions were 1.0 mM in Zn(II) and 0.1 M in KCl. Sodium citraconate and sodium nicotinate varied from 0 to 0.05 M. pH was 6.6 ± 0.02. Since this is higher than the pK value of the acid, total concentration is taken as ligand.

Polarograms were recorded at 25 ± 0.5° on an automatic pen recording polarograph CIC (Baroda, India) with a capillary having the following characteristics, m = 2.37 mg/Sec., t = 3.0 sec. at 35 cm. effective height of mercury column. An Elico-digital pH-meter (Model LI-120) was used for pH-measurement.

RESULTS AND DISCUSSION

The reduction of Zn(II) is a two electron step. It was found to be reversible and of diffusion controlled nature in all media,

Binary Systems

Zn(II)-Citraconate Binary System: Half wave potential vs logarithm of the concentration of ligand was a smooth curve, indicating the formation of more than one complex species. Deford and Hume's treatment of the observed polarographic data revealed the formation of three complexes (Table 1, scheme 1)

Zn(II)-Nicotinate Binary System: This system also indicated the formation of successive complexes. The results are given in Table 1 and scheme 1.

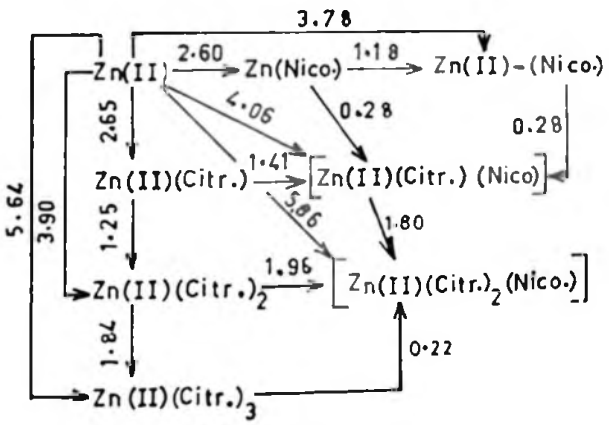
Ternary System

Zn(II)-Citraconate-Nicotinate mixed System: For this study Nicotinate ion concentration was fixed at 0.1 M or 0.2 M whereas the con-

TABLE 1

BINARY SYSTEM VALUES OF $F_1[X]$ FUNCTIONS
Zn(II) = 1.0 mM, μ = 0.1 [KCl],
pH = 6.6 ± 0.02, Temp. 25 ± 0.5°C
$(E_{1/2})_s$ = - 1.10 V vs SCE, i_d = 48

[Ligand (mM)	$-E_{1/2}$	i_d (Div)	$F_0[X]$	$F_1[X]$	$F_2[X]$ X 10^{-2}	$F_3[X]$ X 10^{-5}
Zinc citraconate System						
10	1.122	42	6.37	536	86	-
20	1.131	42	12.85	592	71	-
30	1.144	41	36.33	1177	242	5.4
40	1.152	40	69.52	1713	315	5.8
50	1.156	35	108.6	2152	340	5.2
$\log \beta_1$ = 2.65			$\log \beta_2$ = 3.90		$\log \beta_3$ = 5.64	
Zinc Nicotinate						
10	1.120	44	4.52	352	-	
20	1.130	42	11.89	544	-	
30	1.140	39	27.95	898	166	
40	1.144	38	39.19	954	138	
50	1.150	37	64.30	1266	173	
$\log \beta_1$ = 2.60			$\log \beta_2$ = 3.78			



Scheme 1

centration of citraconate ion was varied, Other conditions were maintained identical to those used for the study of binary systems. Schaap and Mcmaster's method [2] was applied to determine the stoichiometry and formation

TABLE 2

POLAROGRAPHIC CHARACTERISTICS AND $F_{11}[XY]$ FUNCTIONS OF Zn(II)-CITRACONATE-NICOTINATE MIXED SYSTEM
Zn(II) = 1.0 mM; μ = 0.1 [KCl] pH = 6.6±0.02
Temp. = 25 ± 0.5°C $(E_{1/2})_s$ = 1.10 V vs SCE
i_d = 48

[Citraconate] mM	$-E_{1/2}$	i_d (Div)	$F_{00}[X]$	$F_{10}[X]$	$F_{20}[X]$ X 10^{-5}	$F_{30}[X]$ X 10^{-6}
Nicotinic acid = 0.1 M						
10	1.130	38	13.14	-	-	-
20	1.142	36	35.39	1269	-	-
30	1.162	35	173.5	5450	128	1.61
40	1.160	32	302.0	7300	142	1.56
50	1.172	30	441.8	8636	140	1.21
A = 10 B = 1600 C = 80,000 D = 14,000						
Nicotinic acid = 0.2 M						
10	1.132	37	15.77	-	-	-
20	1.150	36	66.09	2304	-	-
30	1.166	33	251.4	7713	173	1.12
40	1.172	32	414.2	9850	183	1.09
50	1.176	29	624.4	12080	190	1.00
A' = 20 B' = 2500 C' = 140000, D' = 100,000						

constants of the ternary complexes. The results are given in Table 2 and scheme 1

Positive value of log K_M (+0.2201) and negative value of log K_S (-0.0809) supports the formation of mixed ligand complexes in solution.

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