POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES OF INDIUM (III) WITH PYRIDINE AND CARBOXYLATE IONS

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Recently Singh et al. [1-2] have studied the mixed complexes of Cd(II), Pb(II) and Eu(III) with pyridine and some carboxylate ions like oxalate, tartrate, succinate, citrate and malonate. Here study of mixed complexes of In(III) with pyridine and carboxylate ions has been reported.

EXPERIMENTAL

Experimental details are as described in ref.2.

RESULTS AND DISCUSSION

In(III) yields a well-defined, diffusion controlled, quasireversible waves (n = 3. slope of the log plot 24-28 mV, k_{sh} = (1×10^{-3} cm/sec) (cf ref. 2).

In(III) with Pyridine, Formate, Maleate and Malonate

It was found that the negative shift in $E_{1/2}$ with pyridine (0.1 M) was maximum at pH 5. Hence the study of In(III) systems with different concentration of ligands was carried out at pH 5. In each case the value of reversible half-wave potential ($E^r_{1/2}$) was obtained by Gellings' method [3]. The plot of $E^r_{1/2}$ vs, log [Py] and log [Mal^{2-}] is a straight line indicating single complexes in these cases. The plots of $E^r_{1/2}$ vs log [$Male^{2-}$] and log [$Forma^-$] are smooth curves. The composition and stability constants of the former system have been determined by Lingane's method [4], while that of the latter by DeFord and Hume's method [5]. Results have been summarised in Table 2.

Mixed Complexes

In the mixed systems, the concentration of carboxylate ion was kept constant, while that of pyridine was varied. In each case the $E_{1/2}$ values were found to be more negative than those obtained in the case of binary systems, thereby showing the formation of mixed complexes. The data has been analysed by the method of Scharp and McMasters [6]. Results are given in Tables 1 and 2.

From the values of these constants, the composition and stability constants of various mixed complex species have been determined and the results have been summarised in Table 2.

The equilibrium constants of disproportionation of the mixed complexes to simple complex in the cases of $[In(Py)_2(Male)]^+$ (-1.63), $[In(Py)_2(Male)_2]^-$ (-2.33), $[In(Py)_3(Male)]^+$ (-6.29), $[In(Py)_2(Mal)_2]^-$ (-5.12), $[In(Py)_2(Forma)]^{2+}$ (-2.93), $[In(Py)_2(Forma)_2]^+$ (-2.1)

TABLE 1

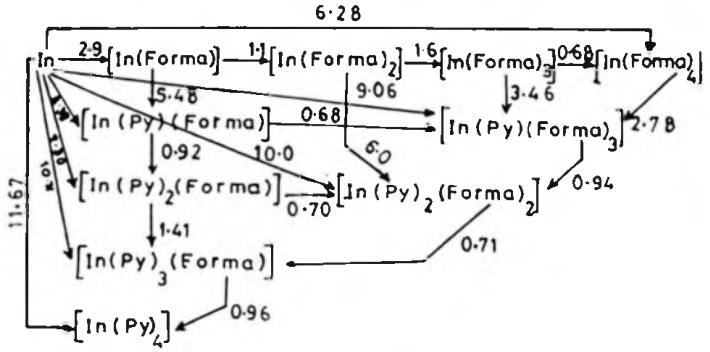
DATA ANALYSED BY SCHAAP AND McMASTERS METHOD
Pyridine cone varied

[Carboxylate]	log of A	B	C	D	E
In-py-Male system					
0.1 M	4.3	7.6	8.78	10.6	11.68
0.2 M	5.3	8.0	9.3	10.95	11.74
In-py-Mal system					
0.05	4.0	7.3	9.26	10.79	11.76
0.1	5.0	7.78	9.78	11.02	11.87
In-py-Formate system					
0.2	4.0	7.6	8.90	10.00	11.68
0.4	5.0	8.0	9.38	10.34	11.88
0.8	6.0	8.7	9.28	10.60	11.88

TABLE 2

System	Stability constant			
In(III)-Py	$\log\beta_4$ = 11.67			
In(III)-$Male^{2-}$	$\log\beta_1$ = 4.30	$\log\beta_2$ = 5.30		
In(III)-Mal^{2-}	$\log\beta_3$ = 7.81			
In(III)-Py-$Male^{2-}$	$\log\beta_{11}$ = 8.48	$\log\beta_{12}$ = 9.00		
	$\log\beta_{21}$ = 9.30	$\log\beta_{22}$ = 10.60		
	$\log\beta_{31}$ = 11.63			
In(III)-Py-Mal^{2-}	$\log\beta_{11}$ = 8.30	$\log\beta_{12}$ = 9.60		
	$\log\beta_{21}$ = 10.08	$\log\beta_{22}$ = 11.68		
	$\log\beta_{31}$ = 12.03			
In(III)-Py-$Forma^-$	$\log\beta_{11}$ = 8.38	$\log\beta_{13}$ = 9.06		
	$\log\beta_{21}$ = 9.30	$\log\beta_{22}$ = 10.00		
	$\log\beta_{31}$ = 10.71			

0013 466 x SN 20 (36) 269-270



Scheme 1

and $[In(py)_3(Forma)]^{2+}$ (-5.75) are all negative this indicating that mixed complexes are favoured over the simple ones.

The variation of degree of formation α_{ij} with increase of [py] shows that the degree of formation of species 1:1:1, 1:1:2, 1:2:1 and 1:2:2 decreases but 1:3:1 increases in cases In-py-Male and In-py-Mal systems. However in case of In-py-Forma system the degree of formation of 1:2:1 and 1:2:2 increases with increase of (py). Otherwise the degree of formation of 1:3:1 increases with [py]. All others decrease with increase of [py].

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