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ELECTROCHEMICAL STUDIES OF INDIUM (III) COMPLEXES AT DIFFERENT TEMPERATURE BY POLAROGRAPHIC TECHNIQUE

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ABSTRACT

Polarographic studies of In (III) complexes with L-tyrosine, citrulline, citraconic acid and hippuric acid have been carried out at two different temperatures using potassium nitrate as supporting electrolytes in aqueous medium. In all the systems, In (III) reduced quasireversibly with the involvement of three electrons. The overall formation constants were determined by DeFord and Hume's method. There was no change in the numbers of species formed by increasing the temperature from 300 K but the stability constant of complex species decreased with the rise in temperature. It was found that stability constants of In (III)-L-tyrosinate system was highest in comparison to other systems.

Key words: Indium (III), L-Tyrosine, Citrulline, Citraconic acid, Hippuric acid.

INTRODUCTION

The survey of literature reveals that researchers have successfully attempted the study of complexation of In (III) by employing various method's[1-6]. Dixit[7] have studied the complexation of indium (III) with (DTA). Carolyn and other researchers have computed the stability constants for complexes of indium (III) using spectrophotometry and complexometry[8-10]. The researchers have also worked on the extraction of indium and synthesis of its complexes with different organic ligands[11,12]. However, the evidence of polarographic investigation of indium (III) with L-tyrosine, citrulline, hippuric acid and citraconic acid were not found. This tempted us to opt for the systematic study of indium (III) with these ligands using polarography. In (III) reduced quasirversibily and hence, for each solution, $E^{r}_{1/2}$ values were obtained by Gellings method. The $E^{r}_{1/2}$ values obtained were used to evaluate stability constants by the DeFord and Hume's method. Mathematical method was also applied to compare the values of stability constants obtained by graphical method of

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DeFord and Hume.

EXPERIMENTAL

The reagents used were of A.R. Grade Purity and all the solutions were prepared in double distilled water. The temperature was kept constant by using Haake-type ultrathermostat. Potassium chloride was used as supporting electrolyte in all the investigations to maintain constant ionic strength. Triton-X-100 was used as maxima suppressor. The capillary had the following characteristic M = 2.38 mg/sec and t = 4.54 sec (in open circuit). Polarograms were recorded manually by plotting current reading on galvanometer against potential applied by the potentiometer in connection with 2.0 volts capacity lead accumulator. All polarograms were recorded after deaeration of the test solutions by passing N_2 gas for 10-15 minutes.

RESULTS AND DISCUSSION

The complexation between metal ion In (III) and ligands was evidenced by the increasing cathodic shifts in half-wave potential and decreasing diffusion currents, observed as the increasing amount of ligand was added to the solution containing In (III) and sufficient amount of KNO_3 to keep the ionic strength of the solution constant.

Gellings method was applied to evaluate the reversible half-wave potential ($E^{r}_{1/2}$) because the slope of 'log plots' indicated the quasireversible nature of reduction. DeFord and Hume's method was used to determine the stability constants. A smooth curve passing almost through the origin was observed on plotting the $F_0[(X)]$ function values against C_x. However, $F_2[(X)]$ values on plotting against C_x, gave a straight line but having slope, which indicated the formation of penultimate complex. The plot between $F_3[(X)]$ and C_x gave a straight line parallel to C_x axis. This denotes the formation of highest stoichiometric complex species. The various stability constants and values at two different temperatures have been recorded in Table 1 and represented graphically in Figs. 1-4.

Table 1: Stability constants of complexes of In (III) at 300 K and 308 K

		DeFord and Hume's		**Mihailov**	
		300 K	**308 K**	**300 K**	**308 K**
Tyrosine	log β_1	2.36	2.19	2.33	2.14

Cont…

		DeFord and Hume's		**Mihailov**	
		300 K	**308 K**	**300 K**	**308 K**
	log β_1	4.59	3.83	4.76	4.01
	log β_1	7.17	6.71	7.01	5.71
Citrulline	log β_1	2.20	2.11	2.17	1.93
	log β_1	3.91	3.61	4.13	1.93
	log β_1	6.17	6.11	5.92	6.33
Citraconic acid	log β_1	2.10	2.03	2.07	1.90
	log β_1	3.60	3.48	3.99	3.71
	log β_1	6.11	6.04	5.74	5.34
Hipppuric acid	log β_1	2.08	2.01	2.07	1.69
	log β_1	3.38	3.32	3.52	3.29
	log β_1	5.25	5.12	4.79	4.72

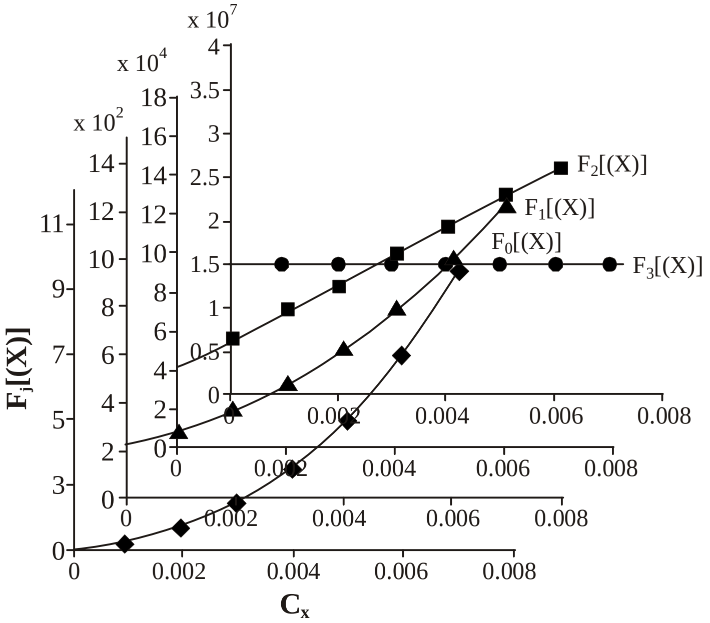


Fig. 1: Plots of $F_j[(X)]$ vs. C_x for In (III) -L-tyrosinate system at 300 K in aqueous medium

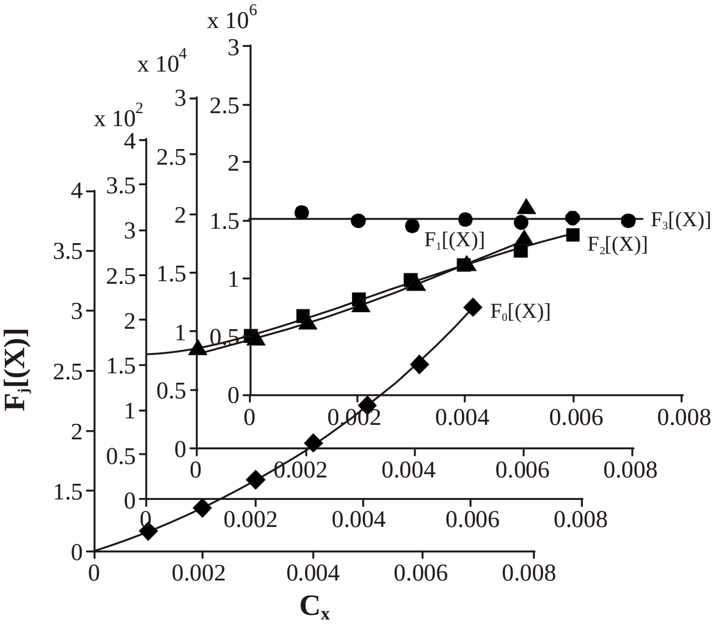


Fig. 2: Plots of $F_j[(X)]$ vs. C_x for In (III) -L-citruline system at 300 K in aqueous medium

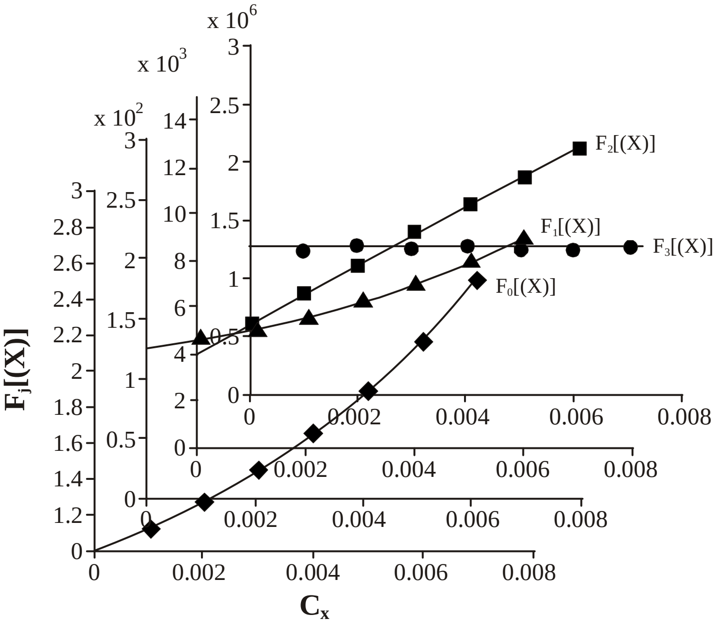


Fig. 3: Plots of $F_j[(X)]$ vs. C_x for In (III) -L-citraconate system at 300 K in aqueous medium

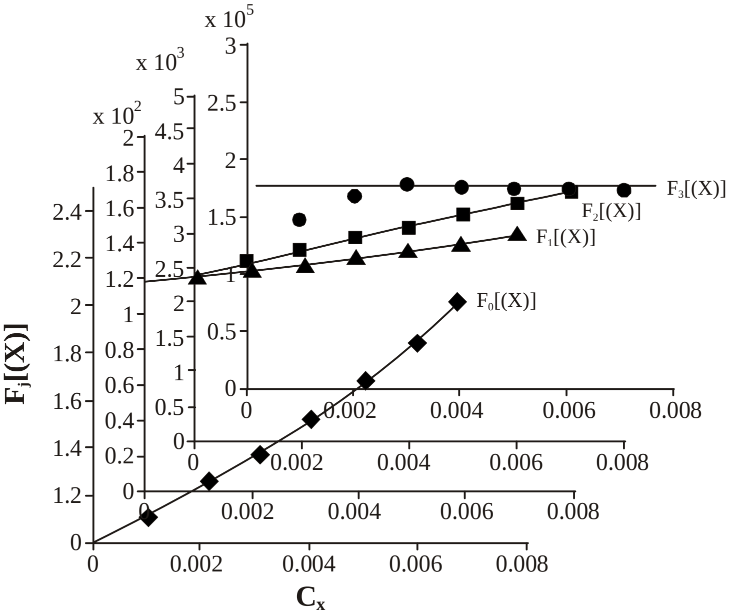


Fig. 4: Plots of $F_j[(X)]$ vs. C_x for In (III)-hippurate system at 300 K in aqueous medium

Table 2

Ligand	**Metal complex species**	**ΔG° (K.Cal/mole)**	**ΔH° (K.cal/mle)**	**ΔS° (Cal/deg/mole)**
L-Tyrosine	1:1	-1.566	-36.062	-0.0749
	1:2	-26.371	-166.351	-0.4666
	1:3	-41.220	-101-012	-0.1993
Citrulline	1:1	-12.645	-18.604	-0.0198
	1:2	-22.460	-64.169	-0.139
	1:3	-35.476	-13.007	+0.0748
Citraconic acid	1:1	-1.104	-15.432	-0.011
	1:2	-20.678	-24.333	-0.012
	1:3	-35.096	-15.480	+0.0653
Hippuric acid	1:1	-11.943	-13.249	-0.006
	1:2	19.414	-13.249	+0.0205
	1:3	-30.156	-28.749	+0.0046

The mathematical method of Mihailov was also applied to verify the formation constants of complexes. Thermodynamic functions have also been evaluated to study the effect of temperature on complexation reaction. The charge in free energy (ΔG°), change in enthalpy (ΔH°) and charge in entropy (ΔS°) are summarized in Table 2.

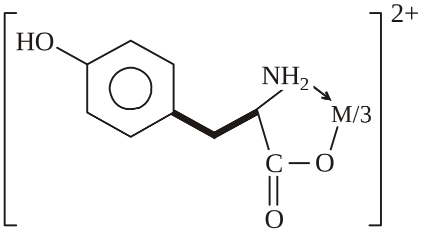
It is shown that the In (III) forms three complexes each with L-tyrosine, citrulline, hippuric acid and citraconic acid. The highest complex species 1 : 3 of In (III) with all four ligands show six coordination numbers of In (III). The donation of electron pair will be from the oxygen atom of carboxylic group and nitrogen atom of amino group.

In case of L-tyrosine, nitrogen of amino group and oxygen of carboxylic group take part in coordination with In (III) and forms five membered chelate ring. In case of citrulline, chelation also occurs but the number of donor atoms are three nitrogen atoms and one oxygen atom, due to which there is uncertainity of number of chelate rings and ring size i.e. five membered, or four membered or eight membered. Due to this uncertainity, citrulline forms weaker complex with metal in comparison to L-tyrosine. Hippuric acid also forms five membered chelate ring with metal as a bidendate ligand but the lone pair present on nitrogen atom are in resonance with oxygen atoms of carbonyl group. Due to this, the availability of lone pair of nitrogen for coordination decreases.

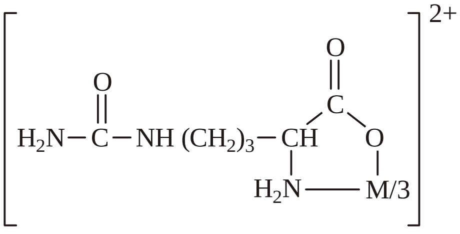
In case of citraconic acid, there is formation of a seven-membered ring. For most stable complexes, the chelated ring should be 5 or 6 membered. On a decrease or increase of ring size of chelates, the stability decreases. So this ligand formed least stable complex with metal in comparison to other three ligands.

CONCLUSION

We can conclude that effect of chelation plays a great role in complexation and their stability. The probable structure of metal ligand complexes are shown below.



(1:1) L-Tyrosine



(1:1) Citrulline

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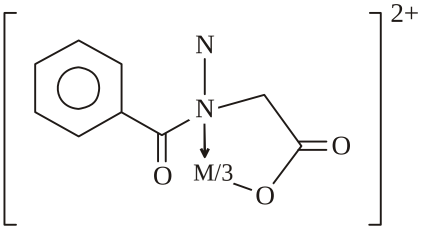
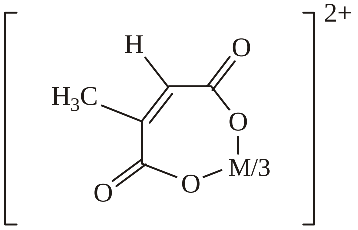


(1:1) Hippuric acid



(1:1) Citraconic acid

M = In (III)

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