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POLAROGRAHIC STUDIES ON THE COMPLEXES OF Ga(III), In(III) AND Tl(I) WITH HISTIDINE

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ABSTRACT

A polarographic studies of Histidine with some P-block elements like Ga(III), In(III) and Tl(I) have been carried out separately at ionic strength kept constant (μ = 1) by using KCl at 298K and 308K temperatures. The reduction of In(III) complexes, Ga(III) complexes and Tl(I) complexes have been found to be quasireversible, irreversible and reversible, respectively in aqueous medium for the same ligand and diffusion controlled involving three electrons in all cases. Ga(III) has shown 1:1, 1:2 and 1:3 complexes, In(III) shows 1:1, 1:2, complexes and Tl(I) shows 1:1 complex with this ligand. DeFord and Hume's method as modified by Irving has been applied for the determination of composition and stability constants of the complex species. Gelling's method was used to calculate $E^r_{1/2}$ values for In(III) complexes. Lingane method was applied to evaluate the stability constant of Tl(I) complexes. The change in thermodynamic parameters ΔG°, ΔH° and ΔS° accompanying complexation have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constants values obtained by graphical method.

Keywords : Polarographic study, In(III), Ga(III), Tl(I), Histidine reversible, quasireversible, irreversible.

INTRODUCTION

The polarographic behaviour of simple[1-4] complexes of various metal ions have been studied at DME. The survey of literature reveals that analyst have successfully attempt the study of complexation of In(III) by employing various methods[5,6]. Electrochemical and thermodynamic behaviour of In(III) complexes have been studied by many workers[7,8,9] at DME. There are scantly constant and thermodynamic parameters of Thallium using polarography. Many workers[10,11] studied thallium(I) complexes with Aza-18-crown-6 in non-aqueous solvents. Kinetic parameters and stability constants of Ga(III) complexes have been studied by many workers[12,13] in aqueous and non-aqueous medium.

The present study deals with the polarographic study of complexes of In(III), Ga(III) and Tl(I) with Histidine in aqueous media at 298K and 308K temperature.

EXPERIMENTAL

A.R. grade chemicals were used. The solution of In(III) and Ga(III) were prepared from their oxides and solution of Tl(I) were prepared from their nitrates.

The DME has the following characteristic m = 1.27 mg/sec and t = 4.12 sec. (in open circuit), constant temperatures (298K and 308K) were maintained using a Haake type thermostat. All the half-wave potentials refer to saturated calomel electrode. Solutions containing 1mM In(III), 1mM Ga(III) or 1mM Tl(I) and various concentrations of Histidine were prepared.

All the polarograms were recorded after de-aeration with purified nitrogen gas.

RESULTS AND DISCUSSION

In each case a single well defined reduction wave appeared. The diffusion currents were found to decrease with increase of ligand concentration as a result of the complex formation. The complex ion formed is of much larger size as compared to the aquo metal ion hence there is the low value of diffusion currents with the increase of ligand concentration. Direact proportionality of the diffusion current to the square root of effective height of mercury column indicate the reduction to be diffusion controlled in each case.

Table-1: Stability constants of Ga(III)-Histidine and In(III)-Histidine complexes

Metal ion	Temp.	log β_j	DeFord and Hume	Mihailov
Ga(III)	298K	log β_1	2.342	2.339
		log β_2	3.447	3.456
		log β_3	4.537	4.398
	308K	log β_1	2.296	2.296
		log β_2	3.389	3.394
		log β_3	4.477	4.316
In(III)	298K	log β_1	4.579	4.624
		log β_2	6.494	6.478
	308K	log β_1	4.531	4.460
		log β_2	6.326	6.452

Table-2: Stability constants and thermodynamic parameters of Ga(III)-Histidine system at 298K in aqueous medium

Metal complex species	log β_j		ΔG°(–)	ΔH°(–)	ΔS°(+)
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	2.342	2.296	3.192	2.003	0.0039
MX_2	3.447	3.389	4.698	2.526	0.0072
MX_3	4.537	4.477	6.184	2.613	0.0119

Table-3: Stability constants and thermodynamic parameters of In(III)-Histidine system at 298K in aqueous medium

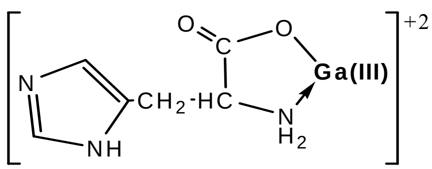
Metal complex species	log β_j		ΔG°(–)	ΔH°(–)	ΔS°(+)
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	4.579	4.531	6.222	2.090	0.013
MX_2	6.494	6.326	8.824	7.318	0.005

Table-4: Stability constants and thermodynamic parameters of Tl(I)-Histidine system at 298K in aqueous medium

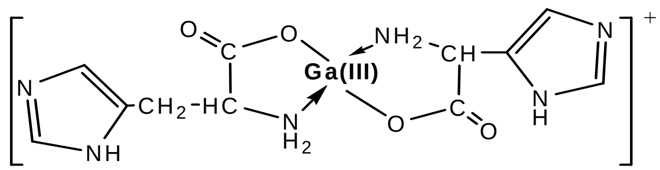
Metal complex species	log β_j		ΔG°(–)	ΔH°(–)	ΔS°(+)
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	2.20	2.02	2.998	7.840	0.036

Possible electronic structure of metal complexes shown below :

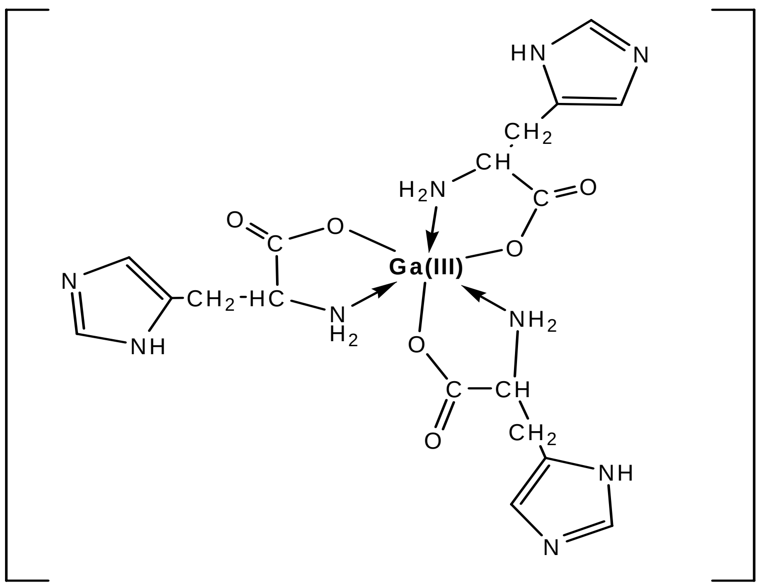
[Ga(III)-(Histidine)] Complexes



[Ga(III)-(Histidinate) $]^{+2}$
1:1 Complex

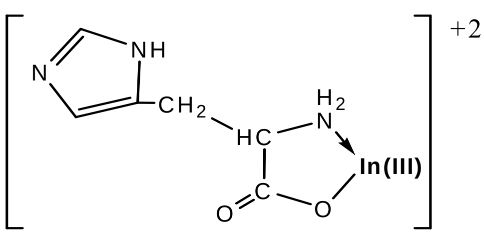


[Ga(III)-(Histidinate)$_2$ $]^{+1}$
1:2 Complex

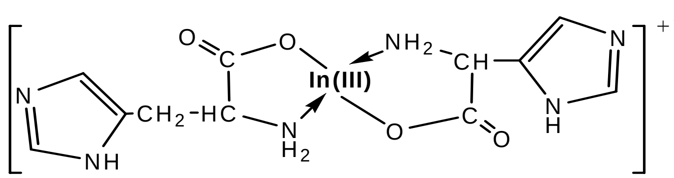


[Ga(III)-(Histidinate)$_3$]
1:3 Complex

[In(III)-(Histidine)] Complexes

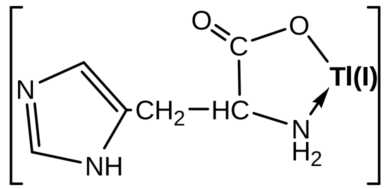


[In(III)-(Histidinate) $]^{+2}$
1:1 Complex



[In(III)-(Histidinate)$_2$ $]^{+1}$
1:2 Complex

[Tl(I)-(Histidine)] Complexes



[Tl(I)-(Histidinate)]
1:1 Complex

The reduction of Ga(III) in Histidine was found irreversible. The values of overall formation constant logβ_j were calculated by the graphical extrapolation method. The experimentally determined values calculated for Ga(III)-Histidine are recorded at 298K and 308K temperatures. The overall formation constants were obtained by extrapolation of $F_j[(X)]$ functions to the zero ligand concentration. The values of stability constants of Ga(III)-Histidine at 298K are logβ_1 = 2.342, log β_2 = 3.447 and log β_3 = 4.537 and at 308K are log β_1 = 2.296, log β_2 = 3.389, log β_3 = 4.477.

In case of In(III) in Histidine was found to be quasireversible. The values of overall formation constant log β_j were calculated by the graphical extrapolation method. The values of stability constants of In(III)-Histidine at 298K are log β_1 = 4.579, log β_2 = 6.494 and at 308K are log β_1 = 4.531, log β_2 = 6.326.

In case of Tl(I)-Histidine system reduction was found reversible and involve one electron transfer. The overall formation constant β_j were a calculated by lingane method. The plot of $-\Delta E_{1/2}$ vs $-\log C_x$ are result in a straight line, signifying the formation of one complex. The number of ligand to metal ion i.e. J, has been determined from the slope of the plot of $\Delta E_{1/2}$ vs $-\log C_x$. Hence, lingane method has been applied to calculate the value of stability constant. The values of stability constants of Tl(I)-Histidine at 298K are logβ_1 = 2.20 and at 308K are logβ_1 = 2.02.

Mihailov's constant 'a' and 'A' have also been calculated for further verification of stability constants given by DeFord and Hume for In(III) and Ga(III) complexes at both temperatures. The overall values to stability constants calculated by both methods for Ga(III) and In(III) complexes are recorded in Table-1 at both temperatures.

The overall changes in thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$, on complex formation have been determined. Thermodynamic parameters for Ga(III)-Histidine, In(III)-Histidine and Tl(I)-Histidine system are recorded in Table-II, III and IV at 298K temperature, respectively.

The more negative value of $\Delta G°$ for 1:3 complex shows that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously. The negative values of $\Delta H°$ suggest that the formation of these complexes is an exothermic process.

It is concluded from above discussion that the complexes formed by Ga(III) with Histidine are more stable than complexes formed by In(III) and Tl(I). Ga(III) attracts ligands more strongly than Indium and Thallium due to smaller size and high charge density.

The order of stability of complexes Ga(III) > In(III) > Tl(I)

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