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STUDY OF REDUCTION OF In (III) WITH PENTANEDIOIC ACID AND 2-(CARBAMIMIDOYLMETHYLAMINO) ETHANOIC ACID AT DROPPING MERCURY ELECTRODE

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ABSTRACT

The study of reduction of In (III) in aqueous solution with pentanedioic acid and 2-(carbamimidoylmethylamino)ethanoic acid was carried out at dropping mercury electrode under varying temperatures at 300 K and 310 K. The constant ionic strength (μ = 1M) has been maintained by using KNO_3 as supporting electrolyte and Triton X-100 was used as maximum suppressor. The stability constants of In (III) with pentanedioic acid and 2-(carbaamimidoylmethylamino)ethanoic acid was evaluated first by DeFord and Hume's method while the stability constants of mixed complexes have been evaluated by the method of Schaap and McMasters. The reduction is found to be reversible and diffusion controlled involving three electrons in each case. The three species of mixed complexes MXY, MX_2Y and MXY_2 have been determined and found to be more stable than that of the simple ones. With the help of these data, the statistical and electrostatic effects have been also studied.

Key words: In (III), Pentanedioic acid, 2-(Carbamimidoylmethylamino)ethanoic acid, Simple and mixed ligand complexes, Polarographic study, DME.

INTRODUCTION

Mixed ligand complexes are usually formed, with a solution containing metal ion with two or more suitable ligands. Mixed ligand complexes have been widely studied due to their analytical applications[1,2] and their possible significant role in biological processes[3-6] and pharmaceutical fields[7-11]. Ternary complexes are important in metal ion catalysed reactions They appear in biological fluids, create specific structures, and manifest themselves as enzyme-metal ion substrate complex. Mixed ligand complexes of Cu (II) have been used in the analysis of semiconductors[12]. Earlier studies on mixed ligand complexes are of spectrophotometeric measurements[13,14]. Studies of mixed ligand complexes of uranyl with pyridoxine and some bicarboxylic acid have been done by Sharma and Chandel[15]. Mixed

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ligand complexes of Cd (II) ion with some amino acid and L-asparginate have been reported by Jangid and Chandel[16]. The study of ternary complexes of different metal ion with amino acids and diocarboxylic acids have been carried out by many workers[17,18]. The survey of literature reveals that there is a lack of data on the mixed ligand complexes of In (III) ion and hence, the present work is undertaken.

EXPERIMENTAL

A d.c. manual polarograph with scale lamp alco type galvanometer, with KCl saturated calomel electrode, copper connecting wires and potentiometer was used. All chemicals used were of AR-grade and all solutions were prepared in double distilled water. The pentanedioic acid and 2-(carbamimidoylmethylamino)ethanoic acid were used as complexing agents and KNO_3 was used as supporting electrolyte to maintain constant ionic strength of the solution and 0.002% Triton X-100 was used as maximum suppressor. The solution under test was maintained at constant temperature using ultra Haake type thermostat. The test solution was placed in an H-type cell coupled with S.C.E. through an agar-agar saturated KCl salt bridge. Purified nitrogen gas was passed through the test solution for 10-15 minutes to remove the dissolved oxygen for polarographic examination. The current variation with reference to applied potential was recorded to obtain the polarogram. In all the systems, the concentration of the weaker ligand was kept constant and that of stronger was varied.

RESULTS AND DISCUSSION

Simple systems

Before the studies of mixed ligand complexes, the formation constants of the complexes of In (III)-pentanedioic acid and In (III)-2-(carbamimidoylmethylamino)ethanoic acid were determined by the method of DeFord and Hume[19]. The values of formation constants of simple systems are recorded in Table 1.

Mixed systems

In (III) forms 1:3 highest complex species with ligands pentanedioic acid and 2-(carbamimidoylmethylamino)ethanoic acid separately. Schaap and McMaster method has been used to determine overall formation constants of mixed ligand complexes formed by In (III) with pentanedioic acid and 2-(carbamimidoylmethylamino)ethanoic acid together with stoichiometry 1:1:1, 1:1:2 and 1:2:1 in same medium as for simple complexes i.e. in aqueous medium. Pentanedioic acid is used as the weaker ligand in the system and 2-

(carbamimidoylmethylamino)ethanoic acid is used as stronger ligand. The two concentrations of the weaker ligand i.e. 0.075M and 0.15M were kept constant and that of stronger ligand was varied from 0.001M to 0.007M All the solutions containing 1 mM of In (III), 0.075M fixed concentration of weaker ligand and adequate amount of 1M KNO_3 to maintain ionic strength constant and 0.002% Triton X-100 was used as maximum suppressor, were taken for experiments and polarographed at varying concentrations of stronger ligand at 300 K and 310 K in first set of observations, and then in second set of observation, all the conditions are kept same except the concentration of weaker ligand, which is kept 0.15M fixed.

Table 1: Stability constants for simple systems in aqueous medium

Systems	Stability constants					
	log β_1		log β_2		log β_3	
	300 K	310 K	300 K	310 K	300 K	310 K
In (III)-Pentanedioic acid	1.698	1.602	2.903	2.698	6.340	6.260
In (III)-2-(Carbamimidoyl methylamino) ethanoic acid	3.301	3.190	6.501	6.458	9.872	9.775

The polarograms were plotted by obtaining current-voltage readings. In each case, a single well defined wave was obtained. The plots of E_{de} vs log i/i_d-i were straight line with a slope of 20-22 mV showing that the three electrons reduction was reversible at D.M.E. at both the temperatures and at both the fixed concentrations of weak ligand. The increase in diffusion current is directly proportional to the square root of the effective height of mercury column indicated that the reduction was entirely diffusion controlled.

A shift in half- wave potential towards more negative side with the increase in stronger ligand concentration was observed. This shift in half-wave potential is greater in the presence of the weaker ligand than in its absence. It signified mixed ligand complex formation. The extended Schaap and Mcmasters[20] treatment was applied to evaluate the F_{00}, F_{10}, F_{20} and F_{30}. Lenden's[21] graphical extrapolation method has been applied on F_{00}, F_{10}, F_{20} and F_{30}, respectively to calculate the values of A, B, C and D at two concentrations of weak ligand for each system. The values of log A, log B, log C and log D are given in the Table 2.

Table 2: Values of constants of In (III)-pentanedioic acid and 2-(carbamimidoylmethylamino) ethanoic acid system at different temperatures

Temperatures	Concentration of weak ligand (fixed)	Log A	Log B	Log C	Log D
300 K	0.15M	3.181	6.362	8.334	10.130
	0.075M	2.634	5.775	8.054	9.952
310 K	0.15M	3.030	6.204	8.253	9.903
	0.075M	2.457	5.580	7.952	9.827

The overall stability constant β_{11}, β_{12} and β_{21} were calculated from the two values of B at two concentrations and are given in Table 3 and from the values of C, values of B_{21} were obtained. The mean value of D is in good agreement with the log β_{30}. These values were obtained by two equations given below:

$$B = \beta_{10} + \beta_{11} [Y] + \beta_{12} [Y]^2 \qquad ….(1)$$

$$C = \beta_{20} + \beta_{21} [Y] \qquad ….(2)$$

Table 3: Stability constants of mixed systems

Metal complex species	log β_{ij}	Temperature	
		300 K	310 K
In (III)-Pentanedioic acid-2-(carbamimidoylmethylamino) ethanoic acid	log β_{11}	5.693	5.526
	log β_{12}	7.995	7.874
	log β_{21}	9.159	9.066

Thermodynamic parameters ΔG^0 and ΔH^0 and ΔS^0, were also calculated for these sets and their values have been recorded in the Table 4.

Table 4: Thermodynamic parameters of mixed In (III)-pentanedioic acid, 2-(carbamimidoyl- methylamino) ethanoic acid

Metal complex Species	ΔG^0 (Kcal mol^{-1})	ΔH^0 (Kcalmol^{-1})	ΔS^0 (Kcalmol^{-1} deg^{-1})
[M(X)(Y)]	-32.7014	-7.1070	0.0853
$[M(X)(Y)_2]^{-2}$	-45.9244	-5.1494	0.1359
$[M(X)_2(Y)]^-$	-52.6106	-3.9578	0.1886

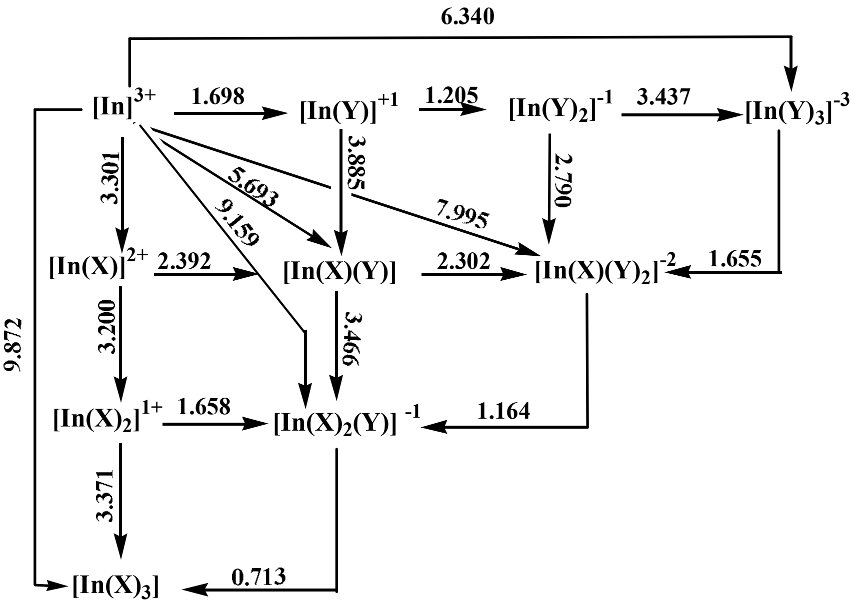
X = 2-(Carbamimidoylmethylamino)ethanoic acid

Y = Pentanedioic acid

M = In (III)

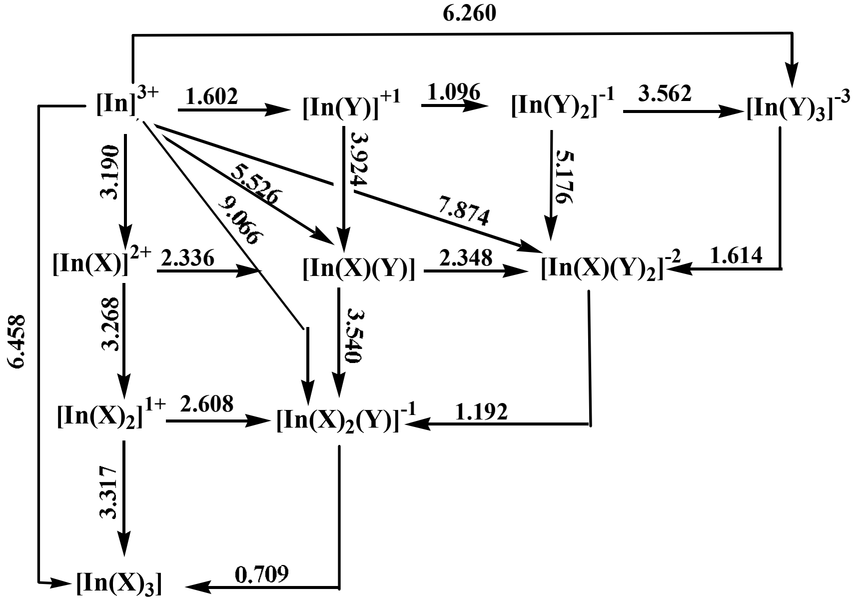
The schematic representation of all the complex species present in the system and the equilibrium amongst them are shown in Schemes 1 and 2.

Scheme 1: In (III)-(pentanedioic acid)-2-(carbamimidoylmethylamino)ethanoic acid at 300 K



Where, X = 2-(Carbamimidoylmethylamino) ethanoic acid and Y = Pentanedioic acid

Scheme 2: In (III)-(pentanedioic acid)-2-(carbamimidoylmethylamino)ethanoic acid at 310 K



Where, X = 2-(Carbamimidoylmethylamino)ethanoic acid and Y = Pentanedioic acid

The mixed ligand complexes formation may also be explained with help of Schemes 1 and 2. The tendency to add [X = 2-(Carbamimidoylmethylamino)ethanoic acid] to In[X] and In[Y] (Y = Pentanedioic acid) can be compared. The logarithm values of stability constants of the above complexes are (3.200, 3.885) and (3.268, 3.924) for In (III)-pentanedioic acid -2-(Carbamimidoylmethylamino)ethanoic acid systems at 300 K and 310 K, respectively.

The tendency to add Y to In[X] and In[Y] can also be compared. The log K values are (2.3929, 1.205) and (2.366, 1.096) at 300 K and 310 K for In (III)- pentanedioic acid - 2-(carbamimidoylmethylamino)ethanoic acid systems, respectively. This indicates that the addition of pentanedioic acid is preffered to In[X] as compared to In[Y].

The log K values for the addition of X = 2-(Carbamimidoylmethylamino)ethanoic acid to In[XY] and In[Y]$_2$ are (3.466, 5.093) and (3.540, 5.176) at 300 K and 310 K for In (III)—pentanedioic acid 2-(carbamimidoylmethylamino)ethanoic acid system, respectively. This indicates that the mixed ligand complexation is favoured.

The log K values for the addition of Y = Pentanedioic acid to In[XY] and In$[X]_2$ are (2.302., 2.658) and (2.348, 2.608) at 300 K and 310 K for In (III)-pentanedioic acid -2-(carbamimidoylmethylamino)ethanoic acid system, respectively. This indicates that the addition of Y is preffered to In$[X]_2$ as compared to In[XY].

For comparing the stability of simple and mixed ligand complexes, it is convenient to measure the mixing constants.

$$K_m = \frac{\beta_{11}}{\sqrt{\beta_{02} \times \beta_{20}}} \quad \ldots(3)$$

and the stabilization constants :

$$\log K_s = \log K_m - \log 2$$

The log K_m values are (0.991and 0.948) and the log K_s values are (0.69 and 0.647) for In (III)-pentanedioic acid-2-(carbamimidoylmethylamino)ethanoic acid systems at 300 K and 310 K, respectively. The positive values of mixing and stabilization constants shows that the ternary complexes are more stable, than the binary complexes.

The tendency to form mixed ligand complexes in solution could be expressed quantitatively in other approach compares the difference in stability (Δ log K), which is the result from the substraction of two constants and must therefore, be a constant. This corresponds to:

$$\Delta \log K = \log K^{AB}_{MAB} - \log K^{M}_{MB} \quad \ldots(4)$$

Since more coordination positions are available for the bonding of the ligand [A]to a given multivalent metal ion than for the second ligand [B].

$$\Delta \log K^{M}_{MB} > \log K^{MA}_{MA_2} \quad \ldots(5)$$

Usually holds i.e. one expects to observe negative values for Δ log K. Another probably more satisfactory manner is to determine statistical values for Δ log K. The statistical values for regular octahedron is 5/12 and Δ log K_{oh} = -0.4; for a square planar, the value of Δ log K= -0.6 and for the distorted octahedron, statistical values i.e. Δ log K lie between - 0.9 to - 0.3.

The Δ log K values can be obtained using the following equations.

$$\Delta \log K_{11} = \log \beta_{11} - (\log \beta_{10} + \log \beta_{01}) \quad \ldots(6)$$

$$\Delta \log K_{12} = \log \beta_{12} - (\log \beta_{10} + \log \beta_{02}) \quad \ldots(7)$$

$$\Delta \log K_{21} = \log \beta_{21} - (\log \beta_{20} + \log \beta_{01}) \quad \ldots(8)$$

The observed values of $\Delta \log K_{11}$, $\Delta \log K_{12}$ and $\Delta \log K_{21}$ are (0.694, 1.791, 0.96) and (0.734, 1.986, 1.006) for In (III)-pentanedioic acid 2-(carbamimidoylmethylamino) ethanoic acid systems at temperatures, 300 K and 310 K, respectively.

The Δ log K values are higher than the statistical values, which again proves that the ternary complexes are more stable than expected from statistical reasons.

CONCLUSION

From these investigations, it has been found that In (III) forms three types of stable complexes with Pentanedioic acid and 2-(carbamimidoylmethylamino)ethanoic acid systems i.e. MXY, MXY_2, MX_2Y. The Δ log K values of these systems are higher than the statistical values, which again prove that these complexes are stable.

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