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Electrochemical studies of Bi(III) complexes with bicarboxylic acids by Deford & Hume's and Mihailov's methods

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ABSTRACT

The reduction of Bi(III) with Bicarboxylic acids(Malonic acid and Adipic acid)is investigated electrochemically in aqueous media at the temperatures 304K and 314K at dropping mercury electrode. The constant ionic strength (μ=1M) has been maintained using KNO_3 as a supporting electrolyte. The reduction of the system in each case is quasireversible and diffusion controlled, involving three electrons. Bi(III) shows 1:1 ,1:2 and 1:3 complexes with these ligands. Gelling's method was used to calculate $E^r_{1/2}$ values for Bi(III) complexes. Thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ were also calculated for the systems. The stability constants of Bi(III) with bicarboxylic acids were calculated by DeFord & Hume method, and have been verified by Mihailov's mathematical approach.

Key words: Bi(III), Malonic acid, Adipic acid, polarographic study, quasireversible, dropping mercury electrode.

INTRODUCTION

Polarography is one of the best technique for the study of coordination compounds in solution and have wide application in various field[1-2]. Many workers have reported the electrochemical[3-5] studies of the metal complexes with some bicarboxylic acids. Spirevska and V. Rekalic[6] have studied the polarographic behaviour of some unsaturated bicarboxylic acids. The complexes of Cd(II) with some bicarboxylic acids have been studied polarographically by many workers[7-10]. Polarographic behaviour of divalent metal ion with many ligands have also been studied Polarographically[11-18] in aqueous media. Bismuth, the heaviest of the group 15 of periodic table elements, occurs on earth in concentrations some what lower than those of Antimony and like Antimony and Arsenic; it is used[19] in many ways.

The present paper deals with the polarographic study of complexes of Bi(III) with Malonic acid and Adipic acid at 304K and 314K in aqueous medium . The thermodynamic functions have also been evaluated to study the effect of temperature on complexation reaction.

EXPERIMENTAL

The reagents were used of A.R. grade and all the solutions were prepared in double distilled water. The test solution was placed in polarographic cell coupled with KCl saturated calomel electrode as reference electrode. The solution under test was maintained at constant temperature using thermostat. Potassium nitrate (KNO_3) was used as supporting electrolyte in all the investigations to maintain constant ionic strength (μ = IM). Solutions containing 0.5mM Bi(III) and various concentrations of sodium salt of the ligands were prepared. The dissolved oxygen was expelled by passing purified nitrogen through the solution. The gradual increase

in current with increase in potential was noted and plotted to obtain the polarogram for the solution.

The capillary of the d.m.e was having the following characteristic at height of mercury column (h_{Hg}) of 100 cm.
m = 4.62 mg / Sec
t = 2 Sec.

RESULTS AND DISCUSSION

Bi(III) forms 1:3 highest complex species with bicarboxylic acid(Malonic acid and Adipic acid) in aqueous media . The concentrations of bicarboxylic acids were varied from 0.001M to 0.008M. The required amount of KNO_3 was added to keep ionic strength constant(μ=1M) The values of half-wave potentials for metal ions and their complexes shifted to more negative value on increasing the concentration of the ligand. The nature of all the waves were quasireversible and diffusion controlled in each case. A plot of $E^r_{1/2}$ vs log [C_x] resulted a smooth curve indicating the formation of successive complexes. DeFord and Hume's[20] method was applied to evaluate the various $F_j[(X)]$ functions values and stability constants. The formation of three complexes were inferred from the plots between $F_j[(X)]$ fuctions values against C_x. The $F_0[(X)]$ and $F_1[(X)]$ plots against C_x, were found to be smooth curves, $F_0[(X)]$ having greater degree of slope than $F_1[(X)]$.

The $F_2[(X)]$ functions values when plotted against concentrations of the ligand, produced a straight line but having some slope. The B_j values were determined as the intercepts on the $F_1[(X)]$, $F_2[(X)]$ and $F_3[(X)]$ functions axis.

Mihailov[21] constants 'a' and 'A' were also evaluated for various combinations of ligand concentrations and at different concentrations of ligands respectively to determine the stability constants mathematically. The values of formation constants are recorded in Tables 1 and 2.

The formation constants were determined at 304K and 314K to study the temperature effect

Table 1: Stability constants of Bi(III) with Malonate and Adipate system in aqueous medium at 304K

Systems	Methods	Stability Constants		
		log β_1	log β_2	log β_3
Bi(III)-Malonate	DeFord and Hume	2.5910	3.7634	6.4248
	Mihailov	2.4561	4.2777	5.9232
Bi(III)-Adipate	DeFord and Hume	2.4149	3.5797	6.2833
	Mihailov	2.3912	4.1149	5.6626

Table 2: Stability constants of Bi(III) with Malonate and Adipate system in aqueous medium at 314K

Systems	Methods	Stability Constants		
		log β_1	log β_2	log β_3
Bi(III)-Malonate	DeFord and Hume	2.4593	3.5563	6.2455
	Mihailov	2.3821	4.1776	5.7971
Bi(III)-Adipate	DeFord and Hume	2.3053	3.4216	6.1522
	Mihailov	2.2724	4.0517	5.6550

A very good agreement can be seen between the values obtained by two methods

Table 3: Stability constants and thermodynamic parameters of Bi(III)-Malonate system at 304K in aqueous medium

Metal complex species	log β_j 304 K	log β_j 314 K	ΔG° (KCal/mole)	ΔH° (KCal/mole)	ΔS° (Cal/mole/K)
MX_1	2.4899	2.4183	-3.4516	-3.1300	1.0579
MX_2	3.6901	3.5365	-5.1154	-6.7109	-5.2486
MX_3	6.3909	6.1958	-8.8593	-8.5193	1.1183

M = Bi(III), X = Malonic Acid

Table 4: Stability constants and thermodynamic parameters of Bi(III)-Adipate system at 304K in aqueous medium

Metal complex species	log β_j 304 K	log β_j 314 K	ΔG° (KCal/mole)	ΔH° (KCal/mole)	ΔS° (Cal/mole/K)
MX1	2.4149	2.3053	-3.3477	-4.7884	-4.7391
MX2	3.5797	3.4216	-4.9624	-6.9094	-6.4047
MX3	6.2833	6.1522	-8.7101	-5.7227	9.8267

M = Bi(III), X = Adipic Acid

on stability of complexes it is found that the formation constants decreased at higher temperature (314K) but the highest complex species remained 1 : 3 with all used ligand.

Malonic acid complexes > Adipic acid complexes

Malonic acid form more stable complex than Adipic acid, because the six membered ring is more stable than the higher membered rings.

The values of thermodynamic parameters (ΔG°, ΔH° and ΔS°) are recorded in Tables 3 and 4. The negative value of free energy change (ΔG°) shows that the reaction is spontaneous. The negative change in enthalpy shows that the reaction is exothermic. The positive values of entropy change is related to the increase in number of particles on complex formation.

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