Electrochemical and Thermodynamic Behaviour of Bi(III) with Oxalic Acid and Malonic Acid at DME in Aqueous Media

M.K. Paliwal and O.D. Gupta*

Department of Chemistry, University of Rajasthan, Jaipur-320 055, India

*Corresponding author: E-mail: gupta_od@yahoo.com; mkpaliwal76@yahoo.com

The reduction of Bi(III) with oxalic acid and malonic acid is investigated polarographically in aqueous medium. Bismuth(III) formed 1:1, 1:2 and 1:3 complexes species with oxalic acid and with malonic acid. The stability constants of Bi(III) with oxalic acid and malonic acid were evaluated by the method of DeFord and Hume. The reduction of the system in each case is quasireversible and diffusion controlled, involving three electrons. The thermodynamic parameters have been determined. The stability constants of these species at 300 K for Bi(III) with oxalic acid are $\log \beta_1 = 2.19$, $\log \beta_2 = 3.90$, $\log \beta_3 = 6.38$ and at 310 K are $\log \beta_1 = 2.41$, $\log \beta_2 = 3.95$, $\log \beta_3 = 6.07$ and thermodynamic parameters free energy (Kcal mol^{-1}), enthalpy (Kcal mol^{-1}) and entropy (cal mol^{-1} deg^{-1}) are -2.87, -46.83 and -0.14 (MX$_1$), -5.12, -43.10 and -0.12 (MX$_2$), -8.37, -40.48 and -0.10 (MX$_3$), respectively. The stability constants of these species at 300 K for Bi(III) with malonic acid are $\log \beta_1 = 1.95$, $\log \beta_2 = 4.00$, $\log \beta_3 = 6.14$ and at 310 K are $\log \beta_1 = 1.78$, $\log \beta_2 = 3.95$, $\log \beta_3 = 6.27$ and thermodynamic parameters free energy (Kcal mol^{-1}), enthalpy (Kcal mol^{-1}) and entropy (cal mol^{-1} deg^{-1}) are -2.56, -38.84 and -0.12 (MX$_1$), -5.25, -42.02 and -0.12 (MX$_2$), -8.06, -43.45 and -0.11 (MX$_3$), respectively. The mathematical Mihailov's method has also been applied for the comparison of stability constants values obtained by graphical method.

Key Words: Polarography, Dropping mercury electrode, Bismuth, Oxalic acid, Malonic acid, Stability constant.

INTRODUCTION

Polarography plays important role in identification of metal ligand complexes. Many workers[1-3] have studied biologically active metal complexes of amino acids which are important in analytical, biochemical and pharmaceutical fields[4-6].

The complexation behaviour of ligand with different metals Cu(II), Zn(II), Ni(II) and Co(II) have been studied by many workers[7-14] but literature is quite silent about the studies of metal ligand complexes of Bi(III) with oxalic acid and malonic acid. Hence the present work has been undertaken for the study. The overall formation constants of the resulting complexes in aqueous medium have been evaluated graphically by DeFord-Hume's method[15]. The overall formation constants of the complexes have also been calculated using mathematical method of Mihailov[16]. Thermodynamics of the complexes has been discussed.

EXPERIMENTAL

A manual polarograph is used to record polarograms, using a saturated calomel electrode as the reference electrode. All the chemicals used were of analytical reagent grade. Oxalic acid and malonic acid were used as complexing agents.

Potassium chloride was used as a supporting electrolyte to maintain the constant ionic strength at 0.1 M. The temperature was maintained constant at 300 ± 1 and 310 ± 1 K with the help of Haak-type ultra thermostat. The capillary with the following characteristics m = 1.96 mg/s, t = 4.10 s/drop (in open circuit) and h$_{eff}$ = 40 cm, was used. Solution of Bi(III) contains concentration of 5×10^{-4} M. Various polarographic measurements and F$_j$[(X)] functions for Bi(III) with oxalic acid and malonic acid have been recorded at 300 and 310 K. Purified nitrogen was used for deaeration.

RESULTS AND DISCUSSION

In each case, a simple well defined reduction wave appeared. The diffusion current was found to decrease with the increase of ligand concentration as a result of the complex formation. The complex ions formed are of much bulky size as compared to the aquo-metal ion, hence there is the low value of diffusion current with increase of ligand concentration.

The values of overall formation constants log β$_j$ were calculated by graphical extraplotation method. For the verification, the mathematical Mihailov's method was also applied to evaluate the stability constants. The graphically determined and mathematically calculated values for Bi(III) with oxalic acid and malonic

acid systems at 300 and 310 K are recorded in Tables 1 and 2, respectively.

TABLE-1
STABILITY CONSTANTS OF Bi(III) OXALIC ACID COMPLEXES

Metal ion	Temp. (K)	$\log \beta_j$	DeFord and Hume	Mihailov
Bi(III)	300	$\log \beta_1$	2.19	2.16
		$\log \beta_2$	3.90	4.21
		$\log \beta_3$	6.38	6.08
	310	$\log \beta_1$	2.71	2.39
		$\log \beta_2$	3.95	4.16
		$\log \beta_3$	6.07	5.75

TABLE-2
STABILITY CONSTANTS OF BI(III) MALONIC ACID COMPLEXES

Metal ion	Temp. (K)	$\log \beta_j$	DeFord and Hume	Mihailov
Bi(III)	300	$\log \beta_1$	1.95	1.91
		$\log \beta_2$	4.00	4.04
		$\log \beta_3$	6.14	6.00
	310	$\log \beta_1$	1.78	1.76
		$\log \beta_2$	3.95	4.06
		$\log \beta_3$	6.27	6.18

The system have been investigated at 300 and 310 K and the thermodynamic functions (ΔG, ΔH and ΔS) have been calculated (Table-3) to understand the temperature effect on the stability of the complexes.

TABLE-3
THERMODYNAMIC FUNCTIONS OF Bi(III)-OXALIC ACID AND Bi(III)-MALONIC ACID COMPLEX SYSTEMS

Metal	Ligand	Complex species	ΔG (–) (Kcal mol^{-1})	ΔH (–) (Kcal mol^{-1})	ΔS (–) (cal mol^{-1} deg^{-1})
Bi(III)	Oxalic acid	MX_1	2.87	46.83	0.14
		MX_2	5.12	43.10	0.12
		MX_3	8.37	40.48	0.10
Bi(III)	Malonic acid	MX_1	2.56	38.84	0.12
		MX_2	5.25	42.02	0.12
		MX_3	8.06	43.45	0.11

M = Bi(III), X = Oxalic acid/malonic acid.

The overall formation constants of consecutive complexes were determined by DeFord and Hume's method at 300 and 310 K. β values were obtained by the graphical method developed by Leden. According to them the function $F_0[(X)]$ may be expressed in the following form:

$$F_0[(X)] = \text{Antilog}\left[0.4343\frac{nF}{RT}\Delta E_{1/2} + \log\frac{I_m}{I_c}\right]$$

I_m and I_c being diffusion current of simple and complex metal ion, respectively.

The $F_0[(X)]$ functions values when plotted against C_x (concentration of ligand), a smooth curve passing almost through the origin was observed. However, $F_1[(X)]$ values on plotting against C_x gave a smooth curve slope, which indicates the formation of complex and the intercept is β_1. The plot of $F_2[(X)]$

values on plotting against C_x gave straight line having slope indicates the formation of the penultimate complex. The $F_3[(X)]$ function values when plotted against C_x gave a straight line parallel to abscissa axis denotes the formation of the highest stoichiometric complex species. The intercept of this line without slope on the ordinate yielded the value of β_3. This proves that the overall formation constant for the formation of 1:3 (metal to ligand) complex.

The functions $F_1[(X)]$, $F_2[(X)]$ and $F_3[(X)]$ are given by following expression:

$$F_N[(X)] = \frac{F_{N-1}[(X)] - \beta_{N-1}}{[(X)]}$$

The values of stability constants have been recorded in Tables 1 and 2. For the verification of these β_j values the mathematical Mihailov's method was also applied to evaluate the stability constants from $F_0[(X)]$ function values. This involves the evaluation of Mihailov's constant 'a' and 'A' for the various ligand concentration, respectively. From the average value of 'a' and 'A' the stability constants have been determined by expression (1).

$$\beta_n = A\frac{a^n}{n!} \tag{1}$$

where n = number of complex formed, which can be known from DeFord and Hume's method.

The value of 'A' and 'a' could be obtained by solving the following two eqn. 2 and 3

$$(F' - 1)\sum_1^n \frac{[X'']^n}{n!}a^{n-1} - (F'' - 1)\sum_1^n \frac{[X']^n}{n!}a^{n-1} = 0 \tag{2}$$

and

$$A = \frac{F' - 1}{\sum_1^n \frac{a^n}{n!}[X]^n} \tag{3}$$

where F' and F" are the vales of the experimental F functions at ligand concentrations X' and X", respectively.

On comparison the overall formations constants determined by both the method are found to be in good agreement. Thermodynamic parameters have also been calculated as the complexation studied at two different temperatures. These parameters ΔG, ΔH and ΔS have been calculated from the following equations

$$\Delta G = -2.303\, RT \log \beta_n \tag{4}$$

$$\frac{\log(\beta_n)_{T_2}}{\log(\beta_n)_{T_1}} = \frac{\Delta H(T_2 - T_1)}{4.576 T_1 T_2} \tag{5}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

where R = gas constant $(\beta_n)_{T_1}$ and $(\beta_n)_{T_2}$ = β_n values at T_1 K and T_2 K, respectively.

The values of these parameters are given in Table-3. The negative value of ΔG shows that the reaction tends to proceed spontaneously. The negative value of (ΔH) indicate the exothermic nature of the reaction process in fair agreement with increasing stability suggesting lower temperature favours the chelation process. The entropy values indicates that the complexation is favoured by enthalpy and entropy factors.

Conclusion

It is seen from the results that Bi(III) forms three complexes with oxalic acid and malonic acid in aqueous medium. Thus in the formation of complexes with Bi(III) of ligands oxalic acid and malonic acid both a single well defined diffusion controlled reduction wave appeared in each case. From the above results, it can be concluded that the formation constant goes on decreasing from oxalic acid to malonic acid. This may be due to the dissociation constants of these acids and the structures of the chelating rings. As we know five and six membered rings are most stable.

As expected, the temperature should cause the stability of any complex to decrease. This has been found in the present investigations where the stability of all complexes decreased when the temperature was raised.

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