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POLAROGRAPHIC STUDIES OF As (III) AND Sb(III) WITH SERINE

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ABSTRACT

The reduction of As(III) and Sb(III) with serine is investigated polarographically in aqueous medium. As(III) and Sb(III) formed 1:1, 1:2 and 1:3 complex species with Serine. The stability constants of As(III) and Sb(III) with serine 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 300K for As(III) with serine are $\log\beta_1 = 2.17$, $\log\beta_2 = 4.60$, $\log\beta_3 = 6.73$ and at 310 K are $\log\beta_1 = 1.87$, $\log\beta_2 = 4.00$, $\log\beta_3 = 6.55$ and thermodynamic parameters free energy (KCal mol^{-1}), enthalpy (KCal mol^{-1}) and entropy (Cal mol^{-1} deg^{-1}) are -2.84, -36.67 and -0.12 (MX_1), -6.04, -37.00 and -0.10 (MX_2), -8.83, -41.41 and -0.10 (MX_3) respectively. The stability constants of these species at 300K for Sb(III) with Serine are $\log\beta_1 = 1.59$, $\log\beta_2 = 4.00$, $\log\beta_3 = 6.41$ and at 310 K are $\log\beta_1 = 2.30$, $\log\beta_2 = 4.34$, $\log\beta_3 = 6.51$ and thermodynamic parameters free energy (KCal mol^{-1}), enthalpy (KCal mol^{-1}) and entropy (Cal mol^{-1} deg^{-1}) are -2.21, -31.26 and -0.09 (MX_1), -5.69, -39.22 and -0.11 (MX_2), -8.54 -41.90 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.

Keywords: Polarography, Dropping mercury electrode, Arsenic, Antimony, Serine, Stability constant, DeFord and Hume's method, Mihailov's method, Thermodynamic parameters.

INTRODUCTION

Polarography plays very 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] and attract wide attention in different fields of research. The recent work in our laboratory has opened many new areas in the study for biologically important ligands with different metals and their ability of complexation.

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 As(III) and Sb(III) Serine. Hence the resent 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. Tyrosine and Serine were used as complexing agents. Potassium nitrate was used as a supporting electrolyte to maintain the ionic strength at 0.1 M. The temperature was maintained constant at 300 ± 1 K and 310 ± 1 K. The capillary with characteristics $m = 1.96$ mg/s, $t = 4.10$ sec. per drop (in open circuit) and $h_{eff} = 40$ cm, was used. Solution of As(III) and Sb(III) contains concentration of 5×10^{-4} M. The standard experimental techniques were used. The various polarographic measurements and $F_j[(X)]$ functions for As(III) and

Sb(III) with serine have been recorded at 300K and 310K. The temperature was kept constant with the help of Haak-type ultra thermostat. 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 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 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 experimentally determined and mathematically calculated values for As(III) and Sb(III) with serine systems at 300 K and 310 K are given Table I and II, respectively.

The system have been investigated at two temperature *viz.* 300 K and 310 K, the Thermodynamic functions ($\Delta G°$, $\Delta H°$ and $\Delta S°$) have been calculated (given in Table-3) to understand the temperature effect on the stability of the complexes.

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

$$F_0[(X)] = \text{antilog}\,[0.4343\frac{nF}{RT}\Delta E_{1/2} + \log\frac{I_M}{I_C}]$$

I_m and I_c are 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 through the origin was observed. However, $F_1[(X)]$ values on plotting against C_x gave a slope, which indicates 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 concentrations respectively. From the average value of 'a' and 'A' the stability constants have been determined by expression (1).

$$\beta_n = A\frac{a^n}{n!} \qquad (1)$$

Where n is the 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 equations (2 and 3).

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

and

$$A = \frac{F'-1}{\sum_{1}^{n} \frac{a^n}{n!}[X]^n} \quad (3)$$

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 methods are found to be in good agreement.

Thermodynamic parameters have been also calculated as the complexation studied at two different temperatures. These parameters ΔG° (change in free energy), ΔH° (change in enthalpy), ΔS° (change in entropy) have been calculated from the following equations

$$\Delta G = -2.303\ RT \log \beta_n \quad (4)$$

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

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (6)$$

Where R = gas constant

$(\beta_n)_{T_1}$ and $(\beta_n)_{T_2}$ = β_n values at T_1 K & 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°) indicates the exothermic nature of the reaction process in fair agreement with increasing stability suggesting lower temperature favours the chelation process. The entropy values indicate that the complexation is favoured by enthalpy and entropy factors.

CONCLUSION

It is seen from the results that As(III) and Sb(III) form three complexes with serine in aqueous medium. Thus in the formation of complexes of As(III) and Sb(III) with ligand Serine, a single well defined diffusion controlled reduction wave appeared in each case. From the above results, It can be concluded that the formation constant go on decreasing from Arsenic to Antimony. This may be due to the size of these metals and the size of the chelating rings. As we know five and six membered rings are most stable and as the ring size decreases, stability of compound is increased. It can be explained on the basis of Bayer's strain theory.

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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Table-1: Stability constants of As(III)-serine complexes.

Metal ion	Temp.	log β_i	DeFord and Hume	Mihailov
As(III)	300K	log β_1	2.17	2.18
		log β_2	4.60	4.56
		log β_3	6.73	6.78
	310K	log β_1	1.87	1.80
		log β_2	4.00	4.22
		log β_3	6.55	6.47

Table-2: Stability constants of Sb(III)-Serine complexes.

Metal ion	Temp.	log β_i	DeFord and Hume	Mihailov
Sb(III)	300K	log β_1	1.59	1.66
		log β_2	4.00	4.01
		log β_3	6.41	6.36
	310K	log β_1	2.30	2.28
		log β_2	4.34	4.44
		log β_3	6.51	6.41

Table-3: Thermodynamic functions of As(III) and Sb(III)–Serine Complex system.

Metal	Ligand	Complex species	$\Delta G°$ (–) (Kcal mol^{-1})	$\Delta H°$ (–) (Kcal mol^{-1})	$\Delta S°$ (–) (Cal $mol^{-1}deg^{-1}$)
As(III)	Serine	MX_1	2.84	36.67	0.12
		MX_2	6.04	37.00	0.10
		MX_3	8.83	41.41	0.10
Sb(III)	Serine	MX_1	2.21	31.26	0.09
		MX_2	5.69	39.22	0.11
		MX_3	8.54	41.90	0.11

M = As(III)/Sb(III), X = Serine

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