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NOTE

Polarographic Studies of Bi(III) Complexes with α-Alanine and L-Valine at Different Temperatures

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The stability constants of Bi(III) with α-alanine and L-valine have been determined polarographically at 304 and 314 K in aqueous medium. DeFord and Hume's method was used to calculate the stepwise formation constants. The mathematical Mihailov method was also used. The reduction of the system in each case is quasireversible and diffusion controlled involving three electrons. The constant ionic strength (μ = 1 M) has been maintained using KNO_3 as a supporting electrolyte. Gellings method was used to calculate $E^r_{1/2}$ values for Bi(III) complexes. The complexes with metal to ligand ratio as 1:1, 1:2, 1:3 have been formed. The thermodynamic fuctions (ΔGº, ΔHº and ΔSº) have been calculated to understand the temperature effect on the stability of the complexes.

Key Words: Bi(III), α-Alanine, L-Valine, Polarographic study, Quasireversible, Dropping mercury electrode.

The polarographic technique is based on the fact that the reduction potential of metal ions are shifted to more negative values as a result of complex formation. Bismuth(III) compounds have important applications in cosmetics and bismuth(III) is a semiconductor dopant. Bismuth(III) complexes preparations have long been used by physicians and most of the word's production of bismuth(III) complexes is used in the pharmaceutical industry. Amino acids which form stable complexes, have analytical importance in separation of transition metals and rare earths[1]. A study of these complexes is also important in biological chemistry, in that the accumulation of sufficient data on amino acids complexes with metal ions may contribute to a better understanding of the type of linkages involved in metal protein interactions[2]. Complexes of amino acids have been found useful applications in biochemistry and medicine[3]. Amino acids are well known for forming specific chelate compounds with several metal ions[4-7] as these contain side chains donor atoms and they are potentially capable of forming chelate ring with metal ion bound at the α-amino nitrogen. A 5 or 6 membered ring greatly contributes to the stability of the complexes[8,9]. Electrochemical and thermodynamic behaviour of many metal complexes of amino acids have been studied by many workers[10-16] at d.m.e.

The present paper deals with the complexation reactions of Bi(III) with α-alanine and L-valine at two different temperatures (304 and 314 K) in aqueous medium. The thermodynamic fuctions (ΔGº, ΔHº and ΔSº) have also been calculated.

A.R. grade chemicals were used. The test solutions were prepared in measuring flaks of pyrex glass using conductivity water. Various solutions were prepared containing 0.5 mM of Bi(III) and varying concentrations of the ligands from 0.001-0.008 M. KNO_3 was used to maintain ionic strength constant at 1 M. The test solution were placed in polarographic cell coupled with KCl saturated calomel electrode as reference electrode. The solutions under test were maintained at constant temperature using thermostat. Before examining the solutions polarographically, purified nitrogen gas was passed through each solution for 15-20 min to remove dissolved oxygen. 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 characteristics at height of mercury column (h_{Hg}) of 100 cm, m = 4.62 mg/s, t = 2 s.

Bi(III) forms 1:3 highest complex species with α-alanine and L-valine in aqueous media. The concentrations of ligands were varied from 0.001-0.008 M. The required amount of KNO_3 was added to keep ionic strength constant (μ = 1 M). The values of half-wave potentials for metal ions and their complexes shifted to more negative value on increasing the concentration of ligand. The nature of all the waves were quasireversible and diffusion controlled in each case. A plot of $E^r_{1/2}$ *versus* log [C_x] resulted a smooth curve indicating the formation of successive complexes. DeFord and Hume's method was applied to evaluate the various $F_j[(X)]$ functions values and stability constants (Tables 1 and 3). 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 β_j values were determined as the intercepts on the $F_1[(X)]$, $F_2[(X)]$ and $F_3[(X)]$ functions axis.

TABLE-1
STABILITY CONSTANTS OF Bi(III)-α-ALANINE SYSTEM IN AQUEOUS MEDIUM

Methods	Temperature (K)	log β_1	log β_2	log β_3
DeFord and Hume	304	1.4624	4.1889	6.8621
	314	1.4216	4.0644	6.8142
Mihailov	304	1.4225	4.2294	6.8604
	314	1.3096	4.1639	6.8419

A good agreement can be seen between the values obtained by two method. The small deviations in the values may be due to error in graphical extrapolation in DeFord and Hume's method.

TABLE-2
THERMODYNAMIC FUNCTIONS FOR Bi(III)-α-ALANINE SYSTEM

Metal complex species	Log β_j		ΔG° (Kcal/mol)	ΔH° (Kcal/mol)	ΔS° (Cal/mol/K)
	304 K	314 K			
MX_1	1.4624	1.4216	-2.0272	-1.7819	0.8069
MX_2	4.1889	4.0644	-5.8068	-2.0329	12.4142
MX_3	6.8621	6.8142	-9.5124	-2.0916	24.4107

M = Bi(III), X = α-Alanine.

TABLE-3
STABILITY CONSTANTS OF Bi(III)- L-VALINE SYSTEM IN AQUEOUS MEDIUM

Methods	Temperature (K)	log β_1	log β_2	log β_3
DeFord and Hume	304	1.3541	4.0719	6.7767
	314	1.3181	3.9965	6.7193
Mihailov	304	1.2976	4.1227	6.7713
	314	1.2659	4.0648	6.6874

TABLE-4
THERMODYNAMIC FUNCTIONS FOR Bi(III)-L-VALINE SYSTEM

Metal complex species	log β_j		ΔG° (Kcal/mol)	ΔH° (Kcal/mol)	ΔS° (Cal/mol/K)
	304 K	314 K			
MX_1	1.3541	1.3181	-1.8771	-1.5745	0.9955
MX_2	4.0719	3.9965	-5.6445	-3.2922	7.7378
MX_3	6.7767	6.7193	-9.3940	-2.5059	22.6581

M = Bi(III), X = L-valine.

From results, it is seen that Bi(III), forms three complexes with amino acids (α-alanine, L-valine). In the formation of complexes of Bi(III) with ligands (α-alanine, L-valine) act as a bidentate ligand having two donor atoms. Bi(III) form 1:3, the highest complexes with amino acids. The formation constants were determined at 304 and 314 K to study the temperature effect on stability of complexes it is found that the formation constants decreased at higher temperature (Tables 1-4).

From the values of overall formation constants of the complexes of Bi(III) with amino acids (α-alanine, L-valine), it is observed that Bi(III) forms weaker complexes with as L-valine compared to α-alanine due to larger size of L-valine molecule, which might be interfering is closer approach to metal ion and steric hindrance is also grater compare to α-alanine. The change in free energy ΔG°, which shows the stability of a complex, more negative the value of greater is the stability of the complex. Hence if any process is accompanied by a decrease in the ΔG°, it means the system is approaching towards grater stability it is found that the stabilities of the complexes are consistent with the order of free energy change (ΔG°). The value of ΔG° becomes more negative when that of ΔS° become more positive and a more stable complex is formed. The negative values of , ΔH° shows that the reactions are exothermic.

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