



## NOTE

### Comparative Study of Stability Constant Values of As(III) Complexes with Amino Acids

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The study of reduction of As(III) with amino acids (L-valine, isoleucine) has been investigated electrochemically in aqueous medium at d.m.e. The stability constants of As(III) with L-valine and isoleucine have been investigated polarographically at 304 and 314 K in aqueous medium. The complexes of As(III) with these ligands ratio as 1:1, 1:2, 1:3 have been reported. DeFord and Hume's method is used to calculate the stepwise formation constants. The mathematical Mihailov's method was also used. The reduction of the system in each case is quasi-reversible and diffusion controlled involving three electrons. The constant ionic strength ( $\mu = 1$  M) has been maintained using  $\text{KNO}_3$  as a supporting electrolyte. Gellings method was used to calculate  $E'_{1/2}$  values for As(III) complexes. The thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) have been calculated to understand the temperature effect on the stability of the complexes.

**Key Words:** As(III), L-Valine, Isoleucine, d.m.e., Polarographic study.

Many workers<sup>1-4</sup> have determined the stability constants of metal amino acid complexes. The polarographic is one of the best techniques for the study of coordination compound in solution.

In human beings arsenic is a notorious environmental toxicant known as both a carcinogen and an altherogen. In cell culture studies, trivalent arsenic enhanced oxidative stress in a variety of mammalian<sup>5</sup> cells and this association may be closely associated with the development of arsenic related diseases. Arsenic in blood not only associated with an increased level of reactive oxygen radicals but is also inversely related to the antioxidant capacity in plasma of humans. The primary function of amino acid is to serve as building blocks of living organisms. Biologically active metal complexes of amino acids, which are important in analytical, biochemical and pharmaceutical fields<sup>6-8</sup>. Amino acids, which form stable complexes have analytical importance in separation of transition metals and rare earths. A study of these complexes is also important in biological chemistry. Valine, leucine and isoleucine are the essential amino acids for human life. Isoleucine and leucine stimulates the brain in order to produce mental alertness and theonine from normal human serum and complexes of Cu(II) with amino acids have been studied polarographically<sup>9-13</sup>. The stability constants of complexes were calculated by the methods of DeFord<sup>14</sup> and Hume and Mihailov<sup>15</sup>.

The present paper deals with the polarographic study of complexes of As(III) with L-valine and isoleucine in aqueous

medium at 304 and 314 K. The systems are quasi-reversible and the reversible half-wave potentials ( $E'_{1/2}$ ) have been determined by using gellings method. The thermodynamic functions  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  have also been evaluated to know the effect of temperature on the complexation.

A CL-362 polarographic analyzer was used to record polarograms. Using saturated calomel electrode as the reference electrode and d.m.e. used as microelectrode. Reagent grade chemicals were used. Amino acids were used as complexing agents and all solution were prepared in double distilled water. Potassium nitrate was used as a supporting electrolyte to maintain constant ionic strength ( $\mu = 1$  M). The d.m.e. had the characteristics,  $m = 4.62$  mg/s,  $t = 2$  s and height of the mercury column  $h_{\text{eff}} = 100$  cm. Purified  $\text{N}_2$  was used for deaeration.

The complexation between As(III) with L-valine and isoleucine were evidenced by cathodic shift in half-wave potentials and a decrease in the diffusion current as the ligands concentration was increased to the solution containing as 0.5 mM As(III) and  $\text{KNO}_3$ , a supporting electrolyte to maintain constant ionic strength ( $\mu = 1$  M). Current-voltage relationships were obtained. The concentration of amino acids were varied from 0.001-0.008 M. The values of half-wave potentials of arsenic and its complexes shifted to more negative values on increasing the concentrations of ligands. Gellings method was used to evaluate the reversible half-wave potential ( $E'_{1/2}$ ) because the slopes of 'log plots' indicated the quasi-reversible nature of the reduction. DeFord and Hume's method was used to determine

the stability constants (Tables 1 and 2). The formation of three complexes was confirmed by the plot between  $F_j[x]$  and  $C_x$ . The  $F_0[x]$  having greater degree of slope than  $F_1[x]$ . The  $F_2[x]$  function when plotted against concentration of the ligand, gave a straight line with a slope and the plot of  $F_3[x]$  versus ligand concentration ( $C_x$ ) gave a straight line parallel to  $C_x$  axis. This denotes the formation of the highest stoichiometric (1:3) complex species and Mihailov's mathematical approach was applied to evaluate stability constants from  $F_0(x)$  functions values.

Systems	Methods	Stability constants		
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
As(III)-L-Valine	DeFord and Hume	2.5774	5.1906	7.9015
	Mihailov	2.5078	5.2789	7.8740
As(III)-Isoleucine	DeFord and Hume	2.1583	4.7867	7.6912
	Mihailov	1.9801	4.9203	7.6845

Systems	Methods	Stability constants		
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
As(III)-L-Valine	DeFord and Hume	2.3838	4.9960	7.7111
	Mihailov	2.0457	4.8606	7.4994
As(III)-Isoleucine	DeFord and Hume	2.0969	4.6972	7.5845
	Mihailov	1.8728	4.8243	7.5999

The effect of side chain on the stabilities of complexes have been observed. It has been observed that if the length of side chain of an amino acid increases by  $\text{CH}_2$  the stability of complex decreases in the order L-valine complex > isoleucine complex.

Isoleucine forms weaker complexes because the steric hindrance is more than L-valine. This has been found in the present investigations where the stability of all the complexes decreased when the temperature was raised. The change in free energy ( $\Delta G^\circ$ ) which shows the stability of a complex, the value of  $\Delta G^\circ$  becomes more negative when that of  $\Delta S^\circ$  become more positive and a more stable complex is formed. The negative values of  $\Delta H^\circ$  shows that the reactions are exothermic (Tables 3 and 4).

Metal complex species	$\log \beta_i$		$\Delta G^\circ$ (Kcal/mol)	$\Delta H^\circ$ (Kcal/mol)	$\Delta S^\circ$ (Cal/mol/K)
	304 K	314 K			
$\text{MX}_1$	2.5774	2.3838	-3.5729	-8.4599	-16.0755
$\text{MX}_2$	5.1906	4.9960	-7.1953	-8.4976	-4.2836
$\text{MX}_3$	7.9015	7.7111	-10.9533	-8.3183	8.6677

Metal complex species	$\log \beta_i$		$\Delta G^\circ$ (Kcal/mol)	$\Delta H^\circ$ (Kcal/mol)	$\Delta S^\circ$ (Cal/mol/K)
	304 K	314 K			
$\text{MX}_1$	2.1583	2.0969	-2.9919	-2.6843	1.0121
$\text{MX}_2$	4.7867	4.6972	-6.6355	-3.9104	8.9642
$\text{MX}_3$	7.6912	7.5845	-10.6618	-4.6608	19.7402

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