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ELECTROCHEMICAL STUDIES OF As (III) COMPLEXES WITH TYROSINE IN AQUEOUS AND AQUEOUS-NONAQUEOUS MEDIA (DMSO/DMF)

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ABSTRACT

The polarographic determination of stability constants of metal complexes of As (III) with tyrosine at 300 K in various aqueous and aqueous-nonaqueous media, have shown the formation of 1 : 1, 1 : 2 and 1 : 3 complexes. The values of overall stability constants of complexes have been calculated by DeFord and Hume's method, which is further verified by Mihoilov's method. The reduction process was found to be quasireversible and diffusion controlled involving three electrons transfer. It was found that the stability constants of As (III)-tyrosine system in aqueous-nonaqueous medium are less than in aqueous medium.

Key words*:* Electrochemical, Polarography, Dropping Mercury electrode, Aqueous, Aqueous-nonaqueous media, Arsenic, Tyrosine, DeFord and Hume's method, Mihailov's method.

INTRODUCTION

The studies of complexation of metals with various ligands polarographically in aqueous media have been carried out from a long time. However, attempts have also been made from a long time to use nonaqueous solvents. Many Workers[1-6] have studied various metal ligand complexes polarographically using various non-aqueous solvents. The number of electrochemical studies of metal ligand complexes are found to be very useful in various fields such as analytical, biochemical and pharmaceutical[7-9]. Kuppusamy et al.[10] evaluated the electrochemical behavior Co (II) in acetronitrile-water mixture at D.M.E. Kumar et al.[11] have evaluated stability constants of Cd (II) and Pb (II) with macrocyclic polyether in ethanol-water mixtures. Golube[12-14] studied the influence of solvents on the thiocyanato complexes of number of metal ions. Lohiya et al.[15] evaluated the electrochemical studies at D.M.E. of copper-2-amino-lepedine complexes in aqueous 1, 4-dioxan, dimethyl formamide,

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acetonitrile and formamide mixture, but literature is quite silent about the studies of metal ligand complexes of As (III) with tyrosine in aqueous and aqueous-nonaqueous media.

Hence, the present work has been undertaken for the study of As (III) in presence of tyrosine. The overall formation constants of the resulting complexes in aqueous and aqueous-nonaqueous (DMSO/DMF) medium have been calculated graphically by DeFord-Hume's method[16]. The overall formation constants of the complexes have also been calculated using mathematical method of Mihailov[17].

EXPERIMENTAL

All the chemicals used are of reagent grade purity. The solvents used were purified by standard methods. A manual polarographic set up was used for recording polarograms. The dropping mercury electrode had the following characteristics m = 1.96 mg and t = 4.10 sec (in open circuit). The supporting electrolyte used was KCl and requisite amount was added to maintain the ionic strength constant [$\mu = 1.0$M]. A solution of 0.002% Triton X-100 was used as maxima suppressor. The temperature was kept constant using Haake-type ultrathermostat (27±0.02°). Before polarographic measurements, purified nitrogen gas was passed for 10 to 15 minutes, after presaturation with aqueous and non-aqueous solvent mixture to be used in the study. The test solution were taken in conventional H-type cell. Polarograms were plotted manually by observing current reading on galvanometer against potential applied by the potentiometer in connection with 2 volts capacity lead accumulator.

RESULTS AND DISCUSSION

The reduction of As (III) complex with ligand gives a well defined wave. The present study deals with comparative study of simple complexes of As (III)-tyrosine system in aqueous and different percentage of aqueous-nonaqueous media. The non-aqueous solvents used in this study are DMSO and DMF. These solvents have been used in three different percentage compositions *viz* 20%, 40%, 60% with water. All the systems have been studied at 300 K. From the experiments, it has been observed that in all cases, electrode process is diffusion controlled and there is quasireversible reduction involving three electrons. In all aqueous and aqueous-nonaqueous solvents, as the increasing amount of ligand (0.001-0.007) was added to the solution containing arsenic (III), requisite amount of KCl as supporting electrolyte to keep ionic strength constant and sufficient amount of Triton X-100 as maximum suppressor, it has been observed that their is an increase in cathodic shift and decrease in diffusion current. This proves the complexation between metal and ligand in aqueous, aqueous-DMSO (20%, 40%, 60%) mixtures and in aqueous-DMF (20%, 40%, 60%) mixtures. The overall formation constants of consecutive complexes in all media were determined by DeFord and Hume's method at 300 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

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

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), gave a smooth curve passing almost through the origin. However, $F_1[(X)]$ values on plotting against C_x gave a curve, which indicates formation of complex and the intercept is β_1. The plot of $F_2[(X)]$ against C_x gave a straight line having slope indicating 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, which 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, which 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 -

$$F_N[(X)] = \frac{F_{N-1}[(X)] - \beta_{N-1}}{[(X)]} \qquad \ldots(2)$$

The values of stability constants have been recorded in Tables 1 and 2. For the verification of these βj 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 (3).

$$\beta_n = A\frac{a^n}{n!} \qquad \ldots.\ (3)$$

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 (4 and 5)

$$(F'-1)\sum_{1}^{n}\frac{[X'']^{n}}{n!}a^{n-1}-(F''-1)\sum_{1}^{n}\frac{[X']^{n}}{n!}a^{n-1}=0 \quad .... (4)$$

and $$A=\frac{F'-1}{\sum_{1}^{n}\frac{a^{n}}{n!}[X]^{n}} \quad .... (5)$$

where F′ and F″ are the values of the experimental F functions at ligand concentrations X′ and X″, respectively.

On comparison, the overall formations constants determined by both the methods were found to be in good agreements.

Table 1: Stability constants for As (III)-tyrosine system in aqueous and aqueous-DMSO mixtures at 300 K

Metal ion	Complexing agent	Media	log β_j	DeFord and Hume	Mihailov
As (III)	Tyrosine	Water	log β_1	2.96	2.88
			log β_2	5.14	5.39
			log β_3	7.82	7.73
		DMSO (20%)	log β_1	2.96	2.90
			log β_2	5.11	5.31
			log β_3	7.66	7.55
		DMSO (40%)	log β_1	2.60	2.60
			log β_2	4.74	4.75
			log β_3	6.75	6.72
		DMSO (60%)	log β_1	2.55	2.28
			log β_2	4.59	4.48
			log β_3	6.30	6.50

Table 2: Stability constants for As (III)-tyrosine system in aqueous and aqueous-DMF mixtures at 300 K

Metal ion	Complexing agent	Media	log β_j	DeFord and Hume	Mihailov
As (III)	Tyrosine	Water	log β_1	2.96	2.88
			log β_2	5.14	5.39
			log β_3	7.82	7.73
		DMF (20%)	log β_1	2.14	2.12
			log β_2	4.07	4.24
			log β_3	7.38	6.18
		DMF (40%)	log β_1	2.09	2.08
			log β_2	4.60	4.50
			log β_3	6.71	6.74
		DMF (60%)	log β_1	2.11	2.10
			log β_2	4.14	4.19
			log β_3	6.17	6.11

While discussing the effect of the solvent on complex formation, the following points need careful consideration i.e. physical properties and chemical properties of solvent. The physical properties of the solvent, dielectric constant has been thought as the most important. Attempts have been made to correlate pK values of the complexes and the dielectric constants of the solvents but with little success.

The results of the present study show that with the increasing concentration of DMSO, DMF, the stability of the As (III)-tyrosine complexes decrease. The stability decreases on going from aqueous solution to solution in 20% 40% and 60% aqueous-nonaqueous solvent mixtures.

The number of complex species formed remained same in aqueous and aqueous-DMF, aqueous-DMSO. The values of the stability constants have been recorded in Tables 1 and 2.

Thus, we see that DMSO (ε = 46.7) and DMF (ε = 36.7) have very different dielectric Constants, but low as compared to water (ε = 78.3), these solvents affect complex formation in the same direction. The chief factor determining the composition and stability of complex is the chemical nature of the solvent and not the dielectric constants.

The stability decreases slightly on going from aqueous solutions to aqueous-nonaqueous solution mixtures in 20%, 40% and 60%. The results show that in the complex containing a metal-nitrogen bond, the addition of non-aqueous solvent decreases the stability. This may be due to the fact that the basic strength of amines decreases on going from aqueous solution to solution in aqueous-nonaqueous media. Thus, results also agree with the observation, which indicates that the chemical nature of the solvent and complexing agent are important factors, which affect the stabilities.

Chemical properties of the solvent thus seem to be operative in affecting the composition and stability of complexes in solution of the chemical properties; important are the acidic and basic nature of the solvent and solution. Neutral solvents like DMF, have neither strong proton donor tendency nor strong proton accepting tendencies. Such solvents serve principally as the suspending medium for the solute species and itself participates in chemical reaction only to a minor extent. Thus, solvation is the most important factor in affecting complex formation in aqueous-organic (aqueous-nonaqueous) solvent mixtures.

Solvation of a metal ion may occur –

(i) Through ion-dipole interaction between the positive cation and the negative end of the solvent dipole; or

(ii) Through coordinate covalent bonds in which the solvent molecule shares a pair of electrons with the cation.

If solvation occurs through ion interaction, the solvation sheath of the resulting ion may be more simple. Water is a normal liquid in which the solvent molecules are predominantly unassociated and kinetically free. Ion-solvent interaction would be predicted, by virtue of the dipolar properties; much as in water except that the solvation sheath may be more simple. In such a case, the simple metal ion easily coordinate with a ligand and the number and stability of complexes may be expected to increase.

Another possibility is the salvation, which may take place through coordinate covalent bonds. In this case, the solvent molecule will be held more rigidly by the metal ion; thus, hindering coordination with the ligand and the result will be a decrease in the number of complex species and lowering the stability of complexes, with increasing solvent concentration.

This seems to explain the results obtained from the study of As (III)-tyrosine complexes in aqueous mixtures. The solvation of the metal ion through coordinate covalent bonds, the solvents like DMF, is also shown by the fact that the half-wave potentials of As (III) become slightly more negative at higher concentration of these solvents.

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