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DETERMINATION OF STABILITY CONSTANTS OF AS(III) COMPLEXES WITH GLYCINE IN DMF AND DMSO AT DROPPING MERCURY ELECTRODE

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ABSTRACT

Arsenic complexes with Glycine have been investigated polarographically in aqueous-nonaqueous medium at 304K. DeFord and Hume's method is used to calculate the stepwise formation constants, The reduction is found to be quasireversible and diffusion controlled involving three electrons in each case. The complexes with metal to ligand ratio 1;1, 1:2, 1:3 have been reported. The stability constants were also calculated by Mihailov's method for As(III)–Glycine system for different percentages of DMF and DMSO (20%, 40% and 60%). The constant ionic strength (μ=1M) has been maintained using KNO_3 as a supporting electrolyte. Gellings method was used to calculate $E^r_{1/2}$ values for As(III) compl

Keywords: As(III), Glycine, DMF, DMSO, polarographic study, Dropping mercury electrode.

INTRODUCTION

Amino acids are well known for their tendency to form complexes with metals and have great significance in biological, pharmaceutical field and are directly involved in all the metabolic, enzymatic activities in every living being. Polarographic behaviour and metal complexes of several such amino acids or compounds have been investigated by various research workers[1-6].Many workers[7-9] have obtained different results in view of the conflicting reports, This field of work is quite demanding for systematic study on the influence of aqueous-organic solvent mixtures on complex formation.

Polarographic studies of complexes in Methanol and Ethanol have been carried out by Migal and co-workers[10-13] and have shown that there is a sharp increase in the stability of complexes above 80% alcohol concentration, which they attributed to solvation effect.

The present paper deals with the complexation reactions of As (III) and determination of stability constants of various species formed by As (III) with Glycine in aqueous mixtures of DMF, and DMSO at 304K. The measurements have been carried out in 20%, 40% and 60% of aqueous-DMF, and aqueous-DMSO which have been evaluated graphically by DeFord and Hume's method[14] and mathematical Mihailov's[15] method was also applied to evaluate the formation constants to verify the values obtained by graphical method .

EXPERIMENTAL

A CL-362 polarographic analyser was used to record polarograms. Using saturated calomel electrode as the reference electrode and d.m.e. used as microelectrode. A.R. grade chemicals were used. The test solutions were prepared in measuring flasks of pyrex glass using conductivity water. Various solutions were prepared containing 0.5mM of As(III), varying concentrations of Glycine from 0.001M to 0.008M and 20% to 60% DMF and DMSO. KNO_3 was used to maintain ionic strength constant at 1.0M. Nitrogen gas was passed through each solution for 15-20 minutes 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 d.m.e. had the characteristics, m = 4.62 mg/s, t = 2 sec and height of the mercury column h_{eff} = 100 cm.

RESULTS AND DISCUSSION

The complex formation between As(III) and Glycine was evidenced by the increasing cathodic shift in the $E_{½}$ and decrease in the diffusion current $E^r_{½}$ is calculated by Gellings method. The ligand (Glycine) was added successively to the solutions containing 0.5mM As(III) and requisite quantity of KNO_3 to keep the ionic strength constant in different percentages (20%, 40%, and 60%) of DMF and DMSO solvents.
The values of $F_j[(X)]$ functions were calculated by DeFord and Hume's method. Plot of $F_0[(X)]$ vs C_X is a smooth curve, signifying the presence of more than one complex. Other derived functions were determined and plotted until the $F_j[(X)]$ vs C_X becomes parallel to X-axis. In this case $F_3[(X)]$ gives a line parallel to X-axis confirming the formation of three successive complexes 1:1, 1:2 and 1:3.

Table-1: Stability constants of As(III)-Glycine in various percentages of DMF-water mixture by DeFord and Hume method.

Stability Constant	20% DMF	40% DMF	60% DMF
log β_1	3.2201	3.2504	3.2810
log β_2	4.3838	5.4082	5.4602
log β_3	8.6254	8.6518	8.6955

Table-2: Stability constants of As(III)-Glycine in various percentages of DMF-water mixture by Mihailov method.

Stability Constant	20% DMF	40% DMF	60% DMF
log β_1	3.0101	3.0463	3.0946
log β_2	5.9379	5.9709	5.9989
log β_3	8.6897	8.7195	8.7271

Table-3: Stability constants of As(III)-Glycine in various percentages of DMSO-water mixture by DeFord and Hume method.

Stability Constant	20% DMSO	40% DMSO	60% DMSO
log β_1	3.1271	3.1643	3.2068
log β_2	5.2922	5.3053	5.3729
log β_3	8.5027	8.5330	8.5731

Table-4: Stability constants of As(III)-Glycine in various percentages of DMSO-water mixture by Mihailov method.

Stability Constant	20% DMSO	40% DMSO	60% DMSO
log β_1	3.0144	3.1437	3.2628
log β_2	5.9789	6.0529	6.1113
log β_3	8.7674	8.7860	8.7837

The stability constants are higher in aqueous-nonaqueous solvent mixtures than in purely aqueous medium. The greater stability of the complexes in DMF and DMSO than in aqueous medium may again be attributed to the less degree of solvation of the metal ion which is due to lower values of dielectric constant than water (ξ = 78.3) so the electrostatic force of attraction between two ions of opposite charge is considerably greater and hence the complex is more stable in these solvent mixtures than purely aqueous medium. The values of stability constants in aqueous-nonaqueous solvent mixtures decrease in the order DMF > DMSO.

The less values of dielectric constants of DMF and DMSO are responsible for the less solvation of he metal ion in DMF, which in turn, makes the approach of the ligand (Glycine) to occupy a coordination site in the coordination sphere of metal ion easier and hence greater the stability of the complex in DMF than DMSO. The decrease in diffusion current with the increase in the percentage (20% to 60%) of nonaqueous solvent may well be explained with decreasing value of the diffusion coefficient, in aqueous and nonaqueous solvents mixture. It is obvious, that in addition to water molecules, some molecules of the nonaqueous solvent occupy a place in the solvation sphere of the depolarizer. The size of these molecules being greater than the size of water molecules, decreases the value of diffusion coefficient which in turn is responsible for the decrease in diffusion current as the amount of nonaqueous solvent is increased so that adding on nonaqueous solvent as DMF and DMSO decreases the dielectric constant of the medium, resulting in greater attraction force and hence higher stability constants are obtained.

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