Polagrographic studies of In(III) complexes with 2,2'-oxydiacetic acid in (DMSO and DMF) aqueous-nonaqueous media

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ABSTRACT

The polarographic determination of stability constants of metal complexes of In(III) with 2,2´ oxydiacetic acid under varying temperatures, at 300K and 310K and in various aqueous-nonaqueous media, have shown the formation of 1:1 and 1:2 complexes. The values of overall stability constants of complexes have been calculated by DeFord and Hume's method which is further verified by Mihailov's method. The reduction process was found to be reversible and diffusion controlled involving three electron transfer. The change in thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ accompanying complexation have been also evaluated.

Key words: Polarography, DeFord-Hume's method, Mihailov's method, DMSO, D.M.E., In(III) 2,2'-xydiacetic acid.

INTRODUCTION

Polarography plays very important role in identification of metal ligand complexes. Mostly all the polarographic investigations have been carried out in aqueous media and the rare are the reports citing advantages by carrying out such investigations in nonaqueous media. The study of metal complexes in nonaqueous solvents by a polarographic methods has attracted much attention in recent years[1-10]. Literature survey reveals number of polarographic studies on the behavior of ligand and their complexes have been found useful applications in biochemistry and medicine[11].

EXPERIMENTAL

All the chemicals which were used are of reagent grade purity. The stock solution of Indium was prepared from Indium oxide. 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 = 4.56 mg and t = 3.2 Sec (in open circuit). The supporting electrolyte used was KNO_3 and requisite amount was added to maintain the ionic strength constant [μ = 1.0M]. A solution of 0.002% triton X-100 was used as maxima suppressor. The temperature was kept constant using Haake-type ultra-thermostat (27 ± 0.02° and 37 ± 0.02°). Before polarographic measurements for dearation, purified nitrogen gas was passed for 10 to 15 minutes, after presaturation with aqueous and nonaqueous 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 20 volts capacity lead accumulator.

RESULTS AND DISCUSSION

The reduction of In(III) Complex with ligand gives well defined wave. The present study deals with comparative study of simple complexes of In(III)-2,2'-Oxydiacetic acid system in aqueous and different percentage of aqueous and aqueous-nonaqueous media. The nonaqueous solvents used in this study are DMSO and DMF. These solvents have been used in three different percentage *viz* 15%, 30%, 45%, with water. All the systems have been studied at two different temperature *viz* 300K and 310K. From the experiments it has been observed that in all case electrode process is diffusion controlled and there is reversible reduction involving three electrons. This is concluded by observing the constancy of ratio of i_d and $h^{1/2}_{eff}$ for each system and the slopes of log plots of log $i/(i_d$-

i) vs $E_{d.e}$ in the range of 20 ±1 mV at both the temperatures. In all the systems at both the temperatures and in all aqueous-nonaqueous solvents, as the increasing amount of ligand (0.001-0.007) is added to the solution containing indium, requisite amount of KNO_3 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 increase in cathodic shift and decrease in diffusion current. This proves the complexation between metal and ligand in aqueous-DMSO (15%, 30%, 45%) mixture and in aqueous-DMF (15%, 30%, 45%) mixture. The overall formation constants of consecutive complexes in all media were determined by DeFord and Hume's method at 300K and 310K. b values was obtained by the graphical method developed by Leden. The $F_0[(X)]$ functions values when plotted

**Table 1: Stability constants of In(III)-2,2′-Oxydiacetic
acid in aqueous-nonaqueous media**

Solvents	Stability constants			
	log β_1		log β_2	
	300K	310K	300K	310K
DMSO (15%)	4.585	4.525	8.300	8.165
DMSO (30%)	4.681	4.613	8.405	8.268
DMSO (45%)	4.886	4.792	8.605	8.456
DMF(15%)	5.111	5.041	8.794	8.636
DMF (30%)	5.236	5.134	8.894	8.744
DMF (45%)	5.279	5.217	9.000	8.846

**Table 2: Stability constants values of In(III) with 2,2′-Oxydiacetic
acid calculated by Mihailov's method at two different temperatures**

Solvents	Stability constants			
	log β_1		log β_2	
	300K	310K	300K	310K
DMSO (15%)	3.746	3.616	7.373	7.245
DMSO (30%)	3.847	3.724	7.476	7.349
DMSO (45%)	3.942	3.789	7.626	7.481
DMF(15%)	4.161	4.095	7.834	7.723
DMF (30%)	4.262	4.234	7.935	7.842
DMF (45%)	4.492	4.345	8.095	7.947

against C_x (concentration of ligand), a smooth curve passing almost through the origin was observed. The plot of $F_1[(X)]$ against C_x gave a straight line having slope indicates the formation of the penultimate complex and the intercept on the ordinate gave the values of β_1 i.e. the overall formation constant for the formation 1:1 metal to ligand complex. The $F_2[(X)]$ 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_2. This proves that the overall formation constant for the formation of 1:2 (Metal : Ligand) complex. The values of stability constants have been given in Table 1. For the verification 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 concentration respectively. From the average value of 'a' and 'A' the stability constants may be determined by expression.

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

Where n is the number of complex formed, which can be known from DeFord and Hume's method. The values of stability constants calculated by Mihailov's method are given in table 2. From these two tables on comparison the overall formation constants determined by both the methods are found to be in good agreement as shown below.

Table 3: Thermodynamic parameters of In(III)-2,2´ Oxydiacetic acid system

System	Medium	Complex Species	$\Delta G°$(Kcal mol^{-1})	$\Delta H°$(Kcal mol^{-1})	DS°(Kcal deg^{-1} mol^{-1})
In-2,2´- Oxydiacetic acid	DMSO(15%)	MX_1	-26.3369	-2.5534	0.0793
		MX_2	-47.6764	-5.7452	0.1398
	DMSO(30%)	MX_1	-26.8883	-2.8939	0.080
		MX_2	-48.2795	-5.8303	0.1415
	DMSO(45%)	MX_1	-28.0659	-4.0003	0.0802
		MX_2	-49.4283	-6.3410	0.1436
	DMF(15%)	MX_1	-29.3583	-2.979	0.0879
		MX_2	-50.514	-6.724	0.1460
	DMF(30%)	MX_1	-30.0763	-4.3408	0.0858
		MX_2	-51.0884	-6.3835	0.1490
	DMF(45%)	MX_1	-30.3233	-2.6385	0.0923
		MX_2	-51.6973	-6.5537	0.1505

Thermodynamic parameters have been also calculated as the complexation studies at two different temperatures. These parameters $\Delta G°$ (change in free energy), $\Delta H°$ (change in enthalpy) and $\Delta S°$ (Change in entropy) have been calculated by the standard equation.

The values of these parameters are given in table 3. The negative value of $\Delta G°$ shows that the reaction tends to proceed spontaneously. The negative value of $\Delta H°$ indicate the exothermic nature of the reaction process in fair agreement with

increasing stability suggesting lower temperature favours the chelation process. The entropy values indicates that the complexation is favored by enthalpy and entropy factors.

CONCLUSION

It is seen from the results that indium forms two complexes with 2,2'-oxydiacetic acid in both and different composition of aqueous and aqueous-nonaqueous medium. Thus in the formation of complexes with In(III) with ligand oxydiacetic acid

acts as a tridentate ligand. A single well defined diffusion controlled reduction wave appeared in each case. It has been observed that there is always a cathodic shift in the half-wave potential irrespective of the nature of solvent same is also observed as the percentage of organic solvent increases in the mixture. Diffusion current always decrease with increase in percentage of nonaqueous solvents.

The values of the stability constants increases with the increase in the percentage of organic solvents in mixture. While discussing the effect of the solvent on complex formation various physical and chemical properties have been taken in consideration. These various factors are dielectric constant, solution of depolarize, viscosity of media, ion pair formation, the coordinating ability of the solvent molecules and those of supporting electrolyte etc. All these factors influence the stability of a complex of different extent.

All these factors affects but in the present case a part of the results obtained can be explained solely on the basis of the dielectric constant factor i.e. as the dielectric constant decreases the value of the stability of complex increases. The decrease in dielectric constants is responsible for the decreasing solution of the metal ion which in turn makes the approach of the ligand to occupy a coordination site in the coordination sphere of metal ion easier and hence increase the stability of the complex. The dielectrie constants of the organic solvents which have been taken in experiment are DMSO = 47.2, DMF = 38.3. As the dielectric constants of the DMF is low the stability of the complex is greater in this solvent (DMF) as compared to DMSO. The effect of temperature was studied on the nature of reduction and stability constants. The variation of temperature has no effect on the nature of reduction while the value of stability constants decrease with the increase in temperature indicates that lower temperature favours the formation of stable complexes.

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