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ELECTROCHEMICAL STUDIES OF Cd (II) COMPLEXES WITH ITACONIC ACID IN NON-AQUEOUS MEDIA (20%, 40%, 60% DMF) AT DME

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ABSTRACT

Studies of Cd (II) complexes with itaconic acid have been carried out by polarographic method in non-aqueous media (20%, 40%, 60% DMF) under varying temperatures, at 298 K and 308 K in presence of KCl as a supporting electrolyte. The reduction of Cd (II) was found to be reversible in non-aqueous medium for itaconic acid ligand and have shown the formation of 1:1, 1:2 and 1:3 complexes. DeFord and Hume's method as modified by Irving has been applied for the determination of composition and stability constant of the complexes species. The changes in thermodynamic parameters $\Delta H°$, $\Delta G°$ and $\Delta S°$ accompanying complexation have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constant values.

Key words : Cd (II), Itaconic acid, Stability constants, Polarographic study, DMF (Dimethylformamide)

INTRODUCTION

The use of the polarographic technique for the study of complexation is well kown[1,2]. The polarographic[3-6] study of metal ligand complexes of Cd (II) has been widely made. Polarographic studies on Cd (II) with some bicarboxylic acid have also been carried out[7]. Electrochemical behaviour of Co (II) in acetonitrile-water mixtures at d. m. e. has been studied by Selveraj and coworkers[8]. Sharma and Gupta[9] have reported the electrokinetic study of gallium (III) with DL-α-alanine in aqueous and 25% ethanol at d.m.e. Lohia et al.[10] have studied the copper complexes in aqueous and non-aqueous (DMF, CH_3CN) media at d.m.e. Polarographic study of Cd (II) with crown ethers in non-aqueous solvents has been carried out by Rounaghi and coworkers[11,12]. The electrochemical reduction of itaconic acid did not receive much attention. A detailed study of electrochemical behaviour of itaconic acid in non-aqueous media (20%, 40%, 60% DMF) has been carried out in order to know the nature of the polarographic wave and the

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stability of metal complexes by changing percentage of the solvent.

EXPERIMENTAL

A. R. grade chemicals were used. The solution of Cd (II) were prepared from their nitrates. The capillary characteristic are m = 4.66 mg/sec and t = 3 seconds. The potentials were measured against SCE as reference electrode. Constant temperature (298 K and 308 K) were maintained using a Haake type thermostat. Polarograms were recorded manually by plotting current reading on galvanometer against potential applied by the potentiometer.

Solution of 0.5 mM Cd (II) and various concentrations of itaconic acid and requisite amount of supporting electrolyte were prepared. Solutions were deareated with nitrogen gas before analysis.

RESULTS AND DISCUSSION

The reduction of Cd (II) in presence of itaconic acid was found to be reversible in non-aqueous media (20%, 40%, 60% DMF) (V/V). The plots of id vs $\sqrt{h_{eff}}$ are found to be linear passing through the origin confirming the diffusion controlled nature of the waves in both type of media. The currents were found to decrease with increase in ligand's concentration as a result of complex formation. The complex ion formed is of much larger size as compared to aqua metal ion and hence, the low values of diffusion currents with the increase of ligand concentration.

The values of overall formation constant log β_j were calculated by the graphical extrapolation method. The experimentally determined values for Cd (II)-itaconic acid system in 20% DMF media at 298 K and 308 K are recorded. The overall formation constants were obtained by extrapolation of $F_j[(X)]$ to the zero ligand concentration. The formation constants log β_1, log β_2 and log β_3 of the three complex species are 3.146, 4.740 and 7.235 at 298 K respectively. The same values at 308 K are 3.079, 4.653 and 7.176, respectively.

In 40% DMF (V/V) solvent the overall formation constants for Cd (II)-itaconic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters are recorded at 298 K and 308 K. The formation constant log β_1, log β_2 and log β_3 of the three complex species formed are 3.176, 4.763 and 6.303 at 298 K and the same values at 308 K are 3.130, 4.698 and 6.220 respectively.

In 60% DMF (V/V) solvent the overall formation constants for Cd (II)-itaconic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters are recorded at 298 K and 308 K. The formation constant log β_1, log β_2 and log β_3 of the three complex species formed are 3.217, 4.832 and 7.255 at 298 K and the same values at 308 K are 3.176, 4.792 and 7.240, respectively.

The decrease in diffusion current with the increase in the percentage of nonaqueous solvent may well be explained with decreasing value of the diffusion coefficient, in aqueous and nonaqueous solvents mixture. It is obivious that in addition to water molecules, some molecules of the coordination sphere of the depolariser. The size of these molecules being greater than the size of the aquated metal ions, 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. The higher viscosity of the medium is also, in part, responsible for the decrease in diffusion current.

The overall change in thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ on complex formation for Cd (II)-itaconic acid system in 20%, 40%, 60% DMF media are recorded in Tables 1, 2 and 3, respectively.

Table 1: The stability constants and thermodynamic parameters of Cd (II)-itaconic acid system in 20% DMF solvent mixtures

Metal complex species	log β_j		$\Delta G°(-)$	$\Delta H°(-)$	$\Delta S°(+)$
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.146	3.079	3.975	2.918	0.0035
MX_2	4.740	4.653	4.398	3.789	0.0020
MX_3	7.235	7.176	7.974	2.570	0.0181

The more negative value of $\Delta G°$ for 1:3 complex shows that the driving tendency of the complexation reaction is from left to right and the reaction tends to proceed spontaneously. The negative values of $\Delta H°$ suggest that the formation of these complexes is an exothermic process.

Table 2: The stability constants and thermodynamic parameters of Cd (II)-itaconic acid system in 40% DMF solvent mixtures

Metal complex species	log β_j		ΔG°(–)	ΔH°(–)	ΔS°(+)
	298 K	308 K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.176	3.130	4.328	2.003	0.0078
MX_2	4.763	4.698	6.491	2.831	0.0122
MX_3	6.303	6.220	9.953	3.615	0.0212

Table 3: The stability constants and thermodynamic parameters of Cd (II)-itaconic acid system in 60% DMF solvent mixtures

Metal complex species	log β_j		ΔG°(–)	ΔH°(–)	ΔS°(+)
	298 K	308 K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.217	3.176	4.384	1.785	0.0087
MX_2	4.832	4.792	6.585	1.742	0.0162
MX_3	7.255	7.240	9.888	0.653	0.0309

The values of stability constants for Cd (II)-itaconic acid system in 20%, 40%, 60% DMF solvents have also been further verified by mathematical method given by Mihailov and datas are given in Table 4.

Table 4: DeFord and Hume's and Mihailov's stability constants of Cd (II)-itaconate system

Solvent	Temp.	log β_j	DeFord and Hume	Mihailov
20% DMF	298 K	log β_1	3.146	3.114
		log β_2	4.740	5.098
		log β_3	7.235	6.906
	308 K	log β_1	3.079	3.028
		log β_2	4.653	5.040
		log β_3	7.176	6.865

Solvent	Temp.	log β_j	DeFord and Hume	Mihailov
40% DMF	298 K	log β_1	3.176	3.181
		log β_2	4.763	4.743
		log β_3	6.303	6.129
	308 K	log β_1	3.130	3.126
		log β_2	4.698	5.019
		log β_3	6.220	6.730
60% DMF	298 K	log β_1	3.217	3.178
		log β_2	4.832	5.155
		log β_3	7.255	6.955
	308 K	log β_1	3.176	3.142
		log β_2	4.792	5.127
		log β_3	7.245	6.930

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