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STUDY OF COMPLEX FORMATION BETWEEN ITACONIC ACID AND Cd(II) ION IN AQUEOUS AND NON-AQUEOUS SOLVENTS (40% DMF, 40% DMSO, 40% ETHANOL) USING POLAROGRAPHIC TECHNIQUE (DME)

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ABSTRACT

Studies of Cd (II) complexes with itaconic acid have been carried out by polarographic method in aqueous and non-aqueous media (40% DMSO, 40% DMF, 40% Ethanol) 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 aqueous and 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 ΔH°, ΔG° and ΔS° accompanying complexation have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constants values.

Key words: Cd (II), Itaconic, Stability constants, Polarographic study, 40% Ethanol, 40% DMF (Dimethylformamide), 40% DMSO (Dimethylsulphoxide)

INTRODUCTION

The use of the polarographic technique for the study of complexation is well known[1,2]. The polarographic study of metal ligand complexes of Cd (II) has been widely carried out[3-6]. 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 DME 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. The copper complexes in aqueous and non-aqueous (DMF, CH_3CN) media at d.m.e. have been studied[10]. Polarographic study of Cd (II) with crown ethers in non-aqueous solvents have been carried out by Rounaghi et al.[11,12]. Many workers have studied electrochemical

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behaviour of Co (II) in acetonitrile-water mixtures at DME[13]. Saini et al.[14,15] have studied the complexes of Cd (II) with antibiotic drug at DME in 20% methanol-water and ethanol-water mixtures and complexes of Cu (II) with antibiotic drug at DME in non-aqueous medium. The electrochemical reduction of Itaconic acid did not receive much attention. A detailed study of electrochemical behaviour of itaconic acid in aqueous and non-aqueous media (40%DMSO, 40% DMF, 40% Ethanol) has been carried out in order to know the nature of the polarographic wave and the stability of metal complexes by changing polarity of the solvent.

EXPERIMENTAL

A.R. grade chemicals were used. The solutions of Cd (II) were prepared from nitrate. The capillary characteristics are m = 4.66 mg/sec and t = 3 seconds. The potentials were measured against a SCE as reference electrode. Constant temperatures (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 aqueous and non-aqueous media (40% DMSO, 40% DMF, 40% Ethanol) (v/v). The plots of i_d vs $\sqrt{h_{eff}}$ were found to be linear passing through the origin confirming the diffusion controlled nature of the waves in both types of media. The currents were found to decrease with increase of ligand 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 in ligand concentration.

The values of overall formation constant log β_j were calculated by the graphical extrapolation method. The experimentally determined values calculated for Cd (II)-itaconic acid system in aqueous media at 298 K and 308 K were 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 2.917, 3.627 and 5.851 at 298 K respectively. The same values at 308 K are 2.823, 3.520 and 5.725, respectively.

In 40% DMF (v/v) solvent, the overall formation constant for Cd (II)-itaconic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters were recorded at 298 K and 308 K, respectively. The formation constants 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 40% DMSO (v/v) solvent, the overall formation constant for Cd (II)-itaconic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters were recorded at 298 K and 308 K, respectively. The formation constant log β_1, log β_2 and log β_3 of the three complex species formed are 3.033, 4.612 and 7.176 at 298 K and the same values at 308 K are 3.000, 4.596 and 7.170, respectively.

In 40% ethanol (v/v) solvent, the overall formation constant for Cd (II)-itaconic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters were recorded at 298 K and 308 K, respectively. The formation constants log β_1, log β_2 and log β_3 of the three complex species formed are 3.290, 4.724 and 7.214 at 298 K and the same values at 308 K are 3.255, 4.707 and 7.206, respectively.

It is concluded from the above results that the stability of the complexes decreases with respect to the dielectric constant values of H_2O, DMF, ethanol and DMSO, which are 79, 39.7, 24.3 and 48.9, respectively. The less value of dielectric constant of ethanol (24.3), DMSO (48.9), DMF (39.7) in comparison to H_2O (79) suggests the less solvation of metal ions in ethanol as this ligand approaches metal ion more easily, which explains the greater stability of complexes. The stability constants are higher in mixtures than purely aqueous medium.

The overall change in thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ on complex formation for Cd (II)-itaconic acid system in aqueous and 40% DMSO, 40% DMF, 40% ethanol media are recorded in Tables 1, 2, 3 and 4, respectively.

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.

The values of stability constants for Cd (II)-itaconic acid system in aqueous 40% DMSO, 40% DMF and 40% ethanol solvent have also been further verified by mathematical method given by Mihailov and data are given in Table 5.

Table 1: Stability constants and thermodynamic parameters of Cd (II) itaconic acid system in squeous media

Metal complex species	log β_j		$\Delta G°(–)$	$\Delta H°(–)$	$\Delta S°$
	298 K	**308 K**	**K.cal/mole**	**K.cal/mole**	**K.cal/mole/deg.**
MX_1	2.917	2.823	3.975	4.368	-0.001
MX_2	3.627	3.520	4.398	4.494	-0.0003
MX_3	5.851	5.725	7.974	5.292	0.009

Table 2: Stability constants and thermodynamic parameters of Cd (II) – itaconic acid system in 40% DMSO solvent mixture

Metal complex species	log β_j		$\Delta G°(–)$	$\Delta H°(–)$	$\Delta S°$
	298 K	**308 K**	**K.cal/mole**	**K.cal/mole**	**K.cal/mole/deg.**
MX_1	3.033	3.00	4.133	0.126	0.013
MX_2	4.612	4.596	6.286	0.672	0.023
MX_3	7.176	7.170	9.780	0.252	0.033

Table 3: Stability constants and thermodynamic parameters of Cd(II)-itaconic acid system in 40% DMF solvent mixture

Metal complex species	log β_j		$\Delta G°(–)$	$\Delta H°(–)$	$\Delta S°$
	298 K	**308 K**	**K.cal/mole**	**K.cal/mole**	**K.cal/mole/deg.**
MX_1	3.176	3.130	4.328	1.932	0.008
MX_2	4.763	4.698	6.491	2.730	0.012
MX_3	6.303	6.220	9.953	3.486	0.021

Table 4: Stability constants and thermodynamic parameters of Cd (II) -itaconic acid system in 40% ethanol solvent mixture

Metal complex species	$\log \beta_j$		$\Delta G°(-)$	$\Delta H°(-)$	$\Delta S°$
	298 K	308 K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.397	3.324	4.630	3.066	0.005
MX_2	4.806	4.792	6.550	0.588	0.023
MX_3	7.267	7.259	9.904	0.336	0.032

Table 5: DeFord and Hume's and Mihailov's tability constants of Cd (II)-itaconate system

Solvent	Temp.	$\log \beta_j$	DeFord and Hume	Mihailov
H_2O	298K	$\log \beta_1$	2.917	2.907
		$\log \beta_2$	3.227	4.006
		$\log \beta_3$	5.851	4.929
	308K	$\log \beta_1$	2.823	2.821
		$\log \beta_2$	3.520	3.778
		$\log \beta_3$	5.725	4.559
40% DMSO	298K	$\log \beta_1$	3.033	2.976
		$\log \beta_2$	4.612	5.032
		$\log \beta_3$	7.176	6.912
	308K	$\log \beta_1$	3.000	2.960
		$\log \beta_2$	4.596	5.003
		$\log \beta_3$	7.170	6.669

Cont…

Solvent	Temp.	$\log \beta_j$	DeFord and Hume	Mihailov
40% DMF	298K	$\log \beta_1$	3.176	3.181
		$\log \beta_2$	7.763	4.743
		$\log \beta_3$	6.303	6.129
	308K	$\log \beta_1$	3.130	3.126
		$\log \beta_2$	4.698	5.019
		$\log \beta_3$	6.220	6.730
40% Ethanol	298K	$\log \beta_1$	3.397	2.976
		$\log \beta_2$	4.806	5.032
		$\log \beta_3$	7.267	6.912
	308K	$\log \beta_1$	3.324	3.318
		$\log \beta_2$	4.792	5.194
		$\log \beta_3$	7.259	6.890

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