Electrochemical studies of Cd(II) complexes with Itaconic acid in aqueous and non-aqueous media (20% DMSO) at 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 (20% DMSO) under varying temperatures, at 298K and 308K 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 $\Delta H°$, $\Delta G°$ and $\Delta S°$ accompanying complexation have been evaluated. The mathematical Mihailov's method has also been applied for the comparison of stability constants values.

Key words: Cd(II), Itaconic, Stability constants, Polarographic study, 20% DMSO.

INTRODUCTION

The use of the polarographic technique for the study of complexation is well known[1-2]. The polarographic[3-6] study of metal ligand complexes of Cd(II) has been widely taken. Polarographic studies on Cd(II) with some bicarboxylic acid have been carried out by many workers[7]. Electrochemical behaviour of Co(II) in acetonitrile-water mixtures at DME has been studied by K. Selveraj and coworkers[8]. V. Sharma[9] has reported the electrokinetic study of Gallium(III) with DL-a-Alanine in aqueous and 25% ethanol at d.m.e. Many workers[10] have been 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 have been carried out by G. 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 aqueous and non-aqueous media (20%DMSO) 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 solution of Cd(II) were prepared from their nitrates. 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 (298K and 308K) were used maintained using a Haake type thermostat. Polarograms were recorded manually by plotting current reading on galvanometer against potential applied by the potentiometer. Solution of 0.5mM Cd(II) and various concentrations of Itaconic acid and requisite amount of supporting electroyte were prepared. Solutions were dearated 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 (20% DMSO) (V/V). The plots of i_d 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 of ligands concentration as a result of complex

Table 1: Polarographic measurements and $F_j[(X)]$ function values of Cd(II)-Itaconic acid system at 298K in aqueous medium Ionic strength (μ) = 1.0M (KCl), [Cd(II)] = 0.5 mM, Temp. = 298K.

C_x (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-V vs S.C.E)	$F_0[(X)]$	$F_1[(X)]$ × 10	$F_2[(X)]$ ×10^3	$F_3[(X)]$ × 10^5
0.000	69	0.5780	-	-	-	-
0.001	65	0.5850	1.8330	83.30	6.000	6.55
0.002	64	0.5967	2.6810	84.05	6.750	7.02
0.003	61	0.6113	3.5476	84.95	7.400	6.85
0.004	59	0.6285	4.4386	85.97	8.175	7.07
0.005	57	0.6476	5.3575	87.15	8.900	7.11
0.006	55	0.6683	6.3052	88.42	9.533	6.98
0.007	54	0.6909	7.2951	89.93	10.328	7.11

$\log \beta_1 = 2.917$ $\log \beta_2 = 3.227$ $\log \beta_3 = 5.851$
C_x = Itaconic acid concentration, moles.litre^{-1}

Table 2: Polarographic measurements and $F_j[(X)]$ function values of Cd(II)-Itaconic acid system at 308K in aqueous medium Ionic strength (μ) = 1.0M (KCl), [Cd(II)] = 0.5 mM, Temp. = 308K.

C_x (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-V vs S.C.E)	$F_0[(X)]$	$F_1[(X)]$ × 10	$F_2[(X)]$ ×10^3	$F_3[(X)]$ × 10^5
0.000	71	0.5780	-	-	-	-
0.001	69	0.5844	1.6706	67.0649	3.849	5.31
0.002	67	0.5885	2.3511	67.5558	4.3790	5.30
0.003	66	0.5918	3.0446	68.154	4.9145	5.32
0.004	66	0.5945	3.7554	68.886	5.5174	5.49
0.005	61	0.5958	4.4835	69.670	5.9807	5.32
0.006	60	0.5977	5.2354	70.561	6.5190	5.33
0.007	58	0.5991	6.0132	71.6173	7.0533	5.33

$\log \beta_1 = 2.823$ $\log \beta_2 = 3.520$ $\log \beta_3 = 5.725$
C_x = Itaconic acid concentration, moles. litre^{-1}

Table 3: Polarographic measurements and $F_j[(X)]$ function values of Cd(II)-Itaconic acid system at 298K in 20% DMSO Ionic strength (μ) = 1.0M (KCl), [Cd(II)] = 0.5 mM, Temp. = 308K.

C_x (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-V vs S.C.E)	$F_0[(X)]$	$F_1[(X)]$ × 10^0	$F_2[(X)]$ ×10^3	$F_3[(X)]$ × 10^6
0.000	74	0.5549	-	-	-	-
0.001	72	0.5645	2.1437	1.1437	43.700	-
0.002	72	0.5707	3.4838	1.2419	70.950	14.475
0.003	72	0.5755	5.0627	1.3542	84.744	14.248
0.004	72	0.5795	6.9225	1.4806	95.156	13.289
0.005	72	0.5834	9.3921	1.6784	115.584	14.736
0.006	72	0.5868	12.2560	1.8760	129.333	14.555
0.007	72	0.5900	15.7461	2.1065	143.785	14.540

$\log \beta_1 = 3.041$ $\log \beta_2 = 4.623$ $\log \beta_3 = 7.161$
C_x = Itaconic acid concentration, moles litre^{-1}

formation. The complex ion formed is of much larger size as compared to aqua metal ion, hence the low values of diffusion currents with the increase of ligand concentration.

The values of overall formation constant $\log \beta_j$ were calculated by the graphical extrapolation method. The experimentally determined values calculated for Cd(II)-Itaconic acid system in aqueous media at 298K and 308K are recorded in Tables 1 and II, respectively. The overall formation constants were obtained by extrapolation of $F_j[(X)]$ to the zero ligand concentration. The formation constants $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ of the three complex species are 2.917, 3.227 and 5.851 at 298K respectively. The same values at 308K are 2.823, 3.520 and 5.725, respectively.

In 20% 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 are recorded at 298K and 308K in Table 3 and 4, respectively. The formation constant $\log b_1$, $\log \beta_2$ and $\log \beta_3$ of the three complex species formed are 3.041, 4.623 and 7.161 at 298K and the same values at 308K are 2.977, 4.579 and 7.158 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 and DMSO are 79 and 48.9, respectively. The less value of dielectric constant of DMSO (48.9) in comparision to H_2O (79) suggests the less solvation of metal ions in DMSO due to 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 20% DMSO media are recorded in Tables 5-6, respectively.

Table 4: Polarographic measurements and $F_j[(X)]$ function values of Cd(II)-Itaconic acid system at 308K in 20% DMSO Ionic strength (μ) = 1.0M (KCl), [Cd(II)] = 0.5 mM, Temp. = 308K.

C_x (Moles/Litre)	i_d (divisions)	$E_{1/2}$ (-V vs S.C.E)	$F_0[(X)]$	$F_1[(X)]$ $\times 10^3$	$F_2[(X)]$ $\times 10^3$	$F_3[(X)]$ $\times 10^6$
0.000	77	0.5546	-	-	-	-
0.001	75	0.5636	2.0030	10.03	53.000	15.000
0.002	69	0.5686	3.1673	10.83	66.825	14.412
0.003	53	0.5700	4.5910	11.97	82.333	14.777
0.004	49	0.5732	6.3410	13.35	96.250	14.562
0.005	42	0.5752	8.5110	15.02	110.400	14.480
0.006	39	0.5777	11.2220	17.03	125.500	14.583
0.007	38	0.2809	14.5040	19.29	139.857	14.551

$\log \beta_1 = 2.977$ $\log \beta_2 = 4.579$ $\log \beta_3 = 7.158$
C_x = Itaconic acid concentration, moles. litre^{-1}

Table 5: The stability constants and thermodynamic parameters of Cd(II)-Itaconic acid system in aqueous solvents mixture

Metal Complex Species	$\log \beta_j$		$\Delta G°(-)$ (Kcal/mole)	$\Delta H°(-)$ (Kcal/mole)	$\Delta S°(-)$ (Kcal/deg/mole)
	298K	**308K**			
MX_1	2.917	2.823	3.975	40.646	0.123
MX_2	3.227	3.520	4.398	45.813	0.138
MX_3	5.851	5.725	7.974	41.095	0.111

M = Cd(III), X = itaconic acid

**Table 6: The stability constants and thermodynamic parameters
of Cd(II)-Itaconic acid system in 20% DMSO solvents mixture**

Metal Complex Species	$\log\beta_j$		$\Delta G°(-)$ (Kcal/mole)	$\Delta H°(-)$ (Kcal/mole)	$\Delta S°(-)$ (Kcal/deg/mole)
	298K	**308K**			
MX1	3.505	3.477	4.777	41.664	0.123
MX2	4.832	4.819	6.585	41.887	0.118
MX3	7.274	7.260	9.914	41.919	0.107

M = Cd(II), X = Itaconic acid

**Table 7: Stability constant of Cd(II) -
Itaconate system**

Solvent	Temp.	$\log\beta_j$	DeForn & Hume	Mihailov's
Water	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
20% DMSO	298K	$\log\beta_1$	3.041	2.920
		$\log\beta_2$	4.623	4.914
		$\log\beta_3$	7.161	6.852
	308K	$\log\beta_1$	2.977	2.936
		$\log\beta_2$	4.579	4.984
		$\log\beta_3$	7.158	6.863

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 and 20% DMSO solvent have also been further verified by mathematical method given by Mihailov and datas are given in Table 7.

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