Electrochemical Studies of Cadmium(II) Complexes with Itaconic Acid in Non-Aqueous Media at Dropping Mercury Electrode

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Studies of Cd(II) complexes with itaconic acid have been carried out by polarographic method in non-aqueous (40 % DMSO, 40 % DMF and 40 % ethanol) medium under varying temperatures, at 298 and 308 K in presence of potassium chloride 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 constants values.

Key Words: Cadmium(II), Itaconic acid, Stability constants.

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. Electrochemical behaviour of Co(II) in acetonitrile water mixtures at dropping mercury electrode has been studied by Selveraj and coworkers[7]. Sharma[8] has reported the electrokinetic study of gallium(III) with DL-α-alanine in aqueous and 25 % ethanol in water at dropping mercury electrode (DME). Many workers[9] have been non-aqueous (DMF, CH_3CN) media at DME. Polarographic study of Cd(II) with crown ethers in non-aqueous solvents have been carried out by Rounaghi and coworkers[10,11]. However, little attention has been paid to the electrochemical behaviour of Cd(II) unsaturated dicarboxylate metal complexes in aqueous/non-aqueous media at DME.

EXPERIMENTAL

AR grade chemicals were used. The capillary has the following characteristics m = 4.66 mg/s and t = 3 s (in open circuit), constant temperatures (298 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. All the half wave potentials refer to saturated calomel electrode solution of

0.5 mM Cd(II) and various concentrations of itaconic acid and requisite amount of supporting electroyte were prepared. All the polarograms were recorded after deaeration with purified nitrogen gas.

RESULTS AND DISCUSSION

The reduction of Cd(II) in presence of itaconic acid was found to be reversible in non-aqueous (40 % DMSO, 40 % DMF and 40 % ethanol) medium. Direct proportionality of the diffusion current to the square root of effective height of mercury column indicate the reduction to be diffusion controlled. The currents were found to decrease with increase of ligands concentration as a result of complex 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 40 % ethanol medium at 298 and 308 K are recorded in Tables 1 and 2, respectively. The overall formation constants were obtained by extrapolation of $F_j[(x)]$ to the zero ligand concentration. The formation constant $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ of the three complex species are 3.397, 4.806 and 7.267 at 298 K, respectively. The same values at 308 K are found 3.424, 4.792 and 7.259, respectively.

TABLE-1

POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % ETHANOL AT 298 K

$[Cd(II)] = 0.5$ mM, $\mu = 1$ (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{1/2}$ (-V *vs.* SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^0$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	60	0.5568	–	–	–	–
0.001	59	0.5730	3.5846	2584.60	84.600	20.60
0.002	58	0.5803	6.4048	2702.42	101.210	18.60
0.003	58	0.5854	9.5769	2858.90	119.633	18.54
0.004	57	0.5895	13.2247	3056.17	139.043	18.76
0.005	57	0.5929	17.3836	3276.72	155.344	18.26
0.006	57	0.5960	22.2853	3547.55	174.591	18.43
0.007	56	0.5988	28.0099	3858.55	194.078	18.50

$\log \beta_1 = 3.397$; $\log \beta_2 = 4.806$; $\log \beta_3 = 7.267$; $C_X =$ Itaconic acid concentration.

In 40 % DMSO 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 298 and 308 K in Tables 3 and 4, respectively. The formation constants $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ of the three complex species formed are 3.033, 4.162 and 7.176 at 298 K and the same values at 308 K are 3.00, 4.596 and 7.178, respectively.

TABLE-2
POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR
THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % ETHANOL AT 308 K
[Cd(II)] = 0.5 mM, μ = 1 (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{\frac{1}{2}}$ (-V vs. SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^0$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	62	0.5566	–	–	–	–
0.001	39	0.5664	3.2756	2275.6	75.600	–
0.002	39	0.5738	3.7491	2374.5	87.250	–
0.003	38	0.5790	8.6616	2553.8	117.933	18.64
0.004	38	0.5833	11.9750	2743.7	135.925	18.48
0.005	38	0.5870	15.9477	2989.5	157.908	19.18
0.006	38	0.5902	20.4550	3242.5	173.750	18.62
0.007	37	0.5930	25.7335	3533.3	190.471	18.35

log β_1 = 3.324; log β_2 = 4.792; log β_3 = 7.260; C_X = Itaconic acid concentration.

TABLE-3
POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR
THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % DMSO AT 298 K
[Cd(II)] = 0.5 mM, μ = 1 (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{\frac{1}{2}}$ (-V vs. SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	62	0.5551	–	–	–	–
0.001	60	0.5645	2.1308	11.3080	50.800	–
0.002	60	0.5706	3.4435	12.2175	70.875	14.93
0.003	60	0.5754	5.0126	13.3753	85.843	14.94
0.004	59	0.5795	6.9442	14.8605	101.525	15.12
0.005	59	0.5833	9.3827	16.7654	119.308	15.66
0.006	59	0.5868	12.3850	18.9750	136.250	15.87
0.007	59	0.5899	15.7934	21.1330	147.614	15.23

log β_1 = 3.033; log β_2 = 4.612; log β_3 = 7.176; C_X = Itaconic acid concentration.

TABLE-4
POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR
THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % DMSO AT 308 K
[Cd(II)] = 0.5 mM, μ =1 (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{\frac{1}{2}}$ (-V vs. SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	69	0.5548	–	–	–	–
0.001	66	0.5638	2.056	10.56	56.000	16.500
0.002	60	0.5688	3.279	11.395	69.750	15.125
0.003	46	0.5702	4.764	12.546	84.866	15.122
0.004	42	0.5734	6.606	14.015	100.375	15.218
0.005	36	0.5754	8.894	15.788	115.760	15.252
0.006	36	0.5789	11.743	17.905	131.750	15.375
0.007	35	0.5822	15.142	20.202	145.742	15.177

log β_1 = 3.000; log β_2 = 4.596; log β_3 = 7.178; C_X = Itaconic acid concentration.

The overall formation constant for Cd(II)-itaconic acid system in 40 % DMF was also calculated by graphical method of DeFord and Hume. The values of polarographic parameters were recorded at 298 and 308 K in Tables 5 and 6, respectively. The formation constants $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ of the three complex species formed are 3.176, 4.763 and 7.303 at 298 K and the same values at 308 K are 3.130, 4.698 and 7.220, respectively.

TABLE-5
POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR
THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % DMF AT 298 K
$[Cd(II)] = 0.5$ mM, $\mu = 1$ (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{1/2}$ (-V *vs.* SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^5$
0.000	75	0.5561	–	–	–	–
0.001	73	0.5678	2.5552	15.552	55.200	–
0.002	71	0.5740	4.2220	16.110	55.500	–
0.003	70	0.5784	6.0747	16.915	63.855	19.51
0.004	68	0.5817	8.0618	17.654	66.362	20.90
0.005	66	0.5844	10.2021	18.404	68.084	20.16
0.006	64	0.5866	12.5223	19.203	70.063	20.10
0.007	62	0.5886	15.0055	20.007	71.540	19.34

$\log \beta_1 = 3.176$; $\log \beta_2 = 4.763$; $\log \beta_3 = 6.303$; C_X = Itaconic acid concentration.

TABLE-6
POLAROGRAPHIC MEASUREMENTS AND $F_j[(X)]$ FUNCTION VALUES FOR
THE Cd(II)-ITACONIC ACID SYSTEM IN 40 % DMF AT 308 K
$[Cd(II)] = 0.5$ mM, $\mu = 1$ (KNO$_3$)

C_X (mol/L)	i_d (divisions)	$E_{1/2}$ (-V *vs.* SCE)	$F_0[(X)]$	$F_1[(X)] \times 10^2$	$F_2[(X)] \times 10^3$	$F_3[(X)] \times 10^6$
0.000	79	0.5559	–	–	–	–
0.001	60	0.5641	2.4060	14.06	56.000	–
0.002	48	0.5679	4.0303	15.161	82.575	16.28
0.003	39	0.5702	5.9332	16.444	98.133	16.04
0.004	35	0.5734	8.2698	18.174	116.862	16.71
0.005	31	0.5753	10.9538	19.907	128.152	15.73
0.006	26	0.5771	14.5032	22.505	150.083	16.68
0.007	25	0.5795	18.6248	25.178	166.828	16.68

$\log \beta_1 = 3.130$; $\log \beta_2 = 4.698$; $\log \beta_3 = 7.220$; C_X = Itaconic acid concentration.

It is concluded from the above results that for a definite composition of the non-aqueous mixture, the stability of the complexes decrease with respect to the dielectric constant of the solvents. The dielectric constant values of DMSO, DMF and ethanol are found to be 48.9, 39.7 and 24.3, respectively. The less value of dielectric constant of DMF in comparison to DMSO suggests that the less solvation of metal ions in DMF which explains the greater stability of the complexes.

The overall change in thermodynamic parameters $\Delta H°$, $\Delta G°$ and $\Delta S°$ on complex formation for Cd(II)-itaconic acid system in 40 % ethanol, 40 % DMSO and 40 % DMF solvent mixtures at 298 K are recorded is Tables 7-9, respectively.

TABLE-7
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF Cd(II)-
ITACONIC ACID SYSTEM IN AQUEOUS-ETHANOL (40%) SOLVENTS MIXTURE

Metal complex species	$\log \beta_i$		$\Delta G°(-)$ (Kcal/mol)	$\Delta H°(-)$ (Kcal/mol)	$\Delta S°(-)$ (Kcal/deg/mol)
	298 K	308 K			
MX_1	3.397	3.324	4.630	41.097	0.122
MX_2	4.806	4.792	6.550	41.878	0.118
MX_3	7.267	7.260	9.904	41.959	0.107

M = Cd(II), X = Itaconic acid

TABLE-8
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF
Cd(II)-ITACONATE IN AQUEOUS-DMSO (40 %) SOLVENTS MIXTURE

Metal complex species	$\log \beta_i$		$\Delta G°(-)$ (Kcal/mol)	$\Delta H°(-)$ (Kcal/mol)	$\Delta S°(-)$ (Kcal/deg/mol)
	298 K	308 K			
MX_1	3.033	3.00	4.133	41.543	0.125
MX_2	4.612	4.596	6.286	41.854	0.119
MX_3	7.176	7.170	9.780	41.965	0.108

M = Cd(II), X = Itaconic acid.

TABLE-9
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF
Cd(II)-ITACONIC ACID SYSTEM IN AQUEOUS-DMF (40%) SOLVENTS MIXTURE

Metal complex species	$\log \beta_i$		$\Delta G°(-)$ (Kcal/mol)	$\Delta H°(-)$ (Kcal/mol)	$\Delta S°(-)$ (Kcal/deg/mol)
	298 K	308 K			
MX_1	3.176	3.181	4.328	42.066	0.126
MX_2	4.763	4.743	6.491	41.823	0.118
MX_3	7.303	6.129	9.953	35.248	0.084

M = Cd(II), X = Itaconic acid.

TABLE-10
DEFORD AND HUME'S AND MIHAILOV'S STABILITY
CONSTANTS OF Cd(II)-ITACONATE SYSTEM

Solvent	Temp. (K)	$\log \beta_i$	DeFord and Hume	Mihailov's
40 % Ethanol	298	$\log \beta_1$	3.397	2.976
		$\log \beta_2$	4.806	5.032
		$\log \beta_3$	7.267	6.912
	308	$\log \beta_1$	3.424	3.318
		$\log \beta_2$	4.792	5.194
		$\log \beta_3$	7.259	6.890

40 % DMF	298	log β₁	3.176	3.181
		log β₂	4.763	4.743
		log β₃	6.303	6.129
	308	log β₁	3.130	3.126
		log β₂	4.698	5.019
		log β₃	7.220	6.730
40 % DMSO	298	log β₁	3.033	2.976
		log β₂	4.162	5.032
		log β₃	7.176	6.912
	308	log β₁	3.000	2.960
		log β₂	4.596	5.003
		log β₃	7.178	6.869

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 40 % ethanol, 40 % DMSO and 40 % DMF solvent have also been further verified by mathematical method given by Mihailov and data are given in Table-10.

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