Electrochemical Reduction Of Cd(III) With Itaconic Acid In Non-Aqueous Medium (60% DMF , 60% , Ethanol , 60% DMSO) : A Polarographic Approach

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Abstract : The reduction of Cd(II)-Itaconic acid complexes have been investigated electrochemically in aqueous-nonaqueous medium (60% DMF, 60% Ethanol and 60% DMSO) at varying temperatures 298K and 308K. The reduction of Cd(II) was found to be reversible in nonaqueous medium for itaconic acid ligand and the formation of complexes 1:1, 1:2 and 1:3 have been reported. 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 mathematical Mihailov's method has been also applied for comparison the stability constant values. The changes in the thermodynamic parameters ΔH^o, ΔG^o and ΔS^o accompanying complexation have been evaluated.

Keywords: Cd(II), Itaconic acid, stability constant, reversible, thermodynamic parameters

1. Introduction

Complex forming species in biological materials are numerous e.g. amino acids, peptides, proteins, carboxylic acids, nucleic acid. Since living organisms contains millions of proteins made by simple amino acids. Salts of Cadmium are used commercially in field such as metallurgy, photography and electrochemistry, a few have been used as ascaricides, antiseptics and fungicides. Itaconic acid is a dicarboxylic acid that has a role as a fungal metabollite and human metabolite. It has recently been identified as antimicrobial and immune supportive metabolite in mammalian immune cells.

The use of the polarographic technique for the study of complexation is well known[1-2]. Polarographic studies on Cd(II) with some bicarboxylic acid have been carried out by many workers[3]. Electrochemical behaviour of Co(II) in acetonitrile-water mixtures at DME has been studied by K. Selveraj and Coworkers[4]. V. Sharma[5] has reported the electrokinetic study of Gallium(III) with DL-α-Alanine in aqueous and 25% ethanol 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[6,7]**.** Polarographic study of mixed ligand carboxymethylmerceptosuccincate-Alaninate or Aspartate, glutamate or valinate with Cd(II), Pb(II) and Tl(I) in aqueous-Ethanol media has been carried out by many workers[8]. Many workers[9,10] have determined the stability constants of Tl(I) complexes with amino acid in aqueous and aqueous-nonaqueous media. Electrochemical behaviour of complexes of Cd^{2+} with different types of ligands in aqueous-nonaqueous medium have been reported by many workers.[11,12] Electrochemical and spectral behaviour of binary and ternary complexes of Co(II) with dicynamide and Pyrazine in non-aqueous solvents have been reported by R. Shukla and many coauthors[13]. Electrochemical behaviour of metals with different ligands in aqueous and non-aqueous medium have been reported by many researchers [14-19].

The electrochemical reduction of Itaconic acid did not receive much attention. A detailed study of electrochemical behaviour of Itaconic acid in non-aqueous media (60% DMF, 60% Ethanol, 60% DMSO) in order to know the nature of the polarographic wave and stability of metal complexes by changing the nature of solvent.

2. 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 is (298 K and 308 K) 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 0.5 mM Cd(II) and various concentrations of Itaconic acid and requisite amount of supporting electrolyte were prepared. Solutions were deaerated with nitrogen gas before analysis. (v/v) 60% Ethanol, (v/v) 60% DMF and (v/v) 60% DMSO were used as a non-aqueous solvent for study.

3. Results and Discussion

The reduction of Cd(II) in presence of Itaconic acid was found to be reversible in non aqueous media [(v/v) 60% DMF, (v/v) 60% Ethanol, (v/v) 60% DMSO). 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 each types of media. 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 concentrations.

The values of overall formation constant log Bj were calculated by the graphical method. The experimentally determined values calculated for Cd(II)-Itaconic acid system in 60% DMF media at 298K and 308K are recorded. The overall formation constants were obtained by extrapolation of Fj[(x)] to the zero ligand concentration. The formation constants log β_1, log B_2 and log β_3 of the three complex species are 3.290, 4.724 and 7.214 at 298 respectively. The same values at 308k are 3.253, 4.207 and 7.206 respectively (Table-1).

In 60% 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 are recorded at 298k and 308k. The formation constant log $\beta_{11,}$ log β_2 and log β_3 of the three complex species formed are 3.505, 4.832 and 7.274 at 298k and the same values at 308k are 3.477, 4.819 and 7.260 respectively (Table-2).

The values of overall formation constants log βj were determined experimentally for Cd(II). Itaconic acid system in 60% DMSO (v/v)media at 298k and 308k temperatures are recorded (Table-3). The formation constants log $\beta_{1,}$ log β_2 and log β_3 of the three complex species are 3.096, 4.638 and 4.909 at 298k respectively. The same values at 308k are 3.079, 4.629 and 7.193 respectively.

The effect of nonaqueous solvents on the stability of the complexes depends on several factors such as dietectric constant, viscosity of the media, depolariser, ion pair formation, the coordinating abilities of the nonaqueous solvent molecules and those of supporting electrolyte etc. The decreasing value of dietectric constant of the medium results in less solution of the metal ions Cd(II) and hence the complex is more stable in nonaqueous solvent.

Results of the present study show that the stability of complexes increases on going from aqueous solution to aqueous-nonaqueous solvent mixtures. DMF (36.71), Ethanol (24.55) and DMSO (46.68) have very low value of dielectric constants as compared to water (80).

The overall change in thermodynamic parameters ΔG^o, ΔH^o and ΔS^o on complex formation for Cd(II)-Itaconic acid system in 60% DMF, 60% Ethanol and 60% DMSO media are recorded in Tables-1,2 and 3, respectively.

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

The more negative value of ΔG^o 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 ΔH^o suggest that the formation of these complexes is an exothermic process.

Table-1

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

Metal complex species	log βj		ΔG°(-)	ΔH°(-)	ΔS°
	298k	308k	K.cal/mole	K.cal/mole	K.cal/mole
MX_1	3.290	3.253	4.384	41.465	0.124
MX_2	4.724	4.707	6.585	41.652	0.117
MX_3	7.214	7.206	9.888	41.913	0.107

Table-2

The stability constants and Thermodynamic parameters of Cd(II)-Itaconic acid system in 60% Ethanol solvent mixtures

Metal complex species	log βj		ΔG°(-)	ΔH°(-)	ΔS°
	298k	308k	K.cal/mole	K.cal/mole	K.cal/mole
MX_1	3.505	3.477	4.777	41.664	0.123
MX_2	4.832	4.819	6.585	41.887	0.118
MX_3	7.274	7.260	9.914	41.919	0.107

Table-3

The stability constants and Thermodynamic parameters of Cd(II)-Itaconic acid system in 60% DMSO solvent mixtures

Metal complex species	log βj		ΔG°(-)	ΔH°(-)	ΔS°
	298k	308k	K.cal/mole	K.cal/mole	K.cal/mole
MX_1	3.096	3.079	4.219	41.769	0.126
MX_2	4.638	4.629	6.321	41.864	0.119
MX_3	7.909	7.193	9.840	41.843	0.107

Table-4

The stability constants and Thermodynamic parameters of Cd(II)-Itaconate system

Solvent	Temp.	logβj	DeFord & Hume	Mihailov
60% DMF	298k	$\log\beta_1$	3.290	3.233
		$\log\beta_2$	4.724	5.112
		$\log\beta_3$	7.214	6.816
	308k	$\log\beta_1$	3.253	3.242
		$\log\beta_2$	4.707	5.140
		$\log\beta_3$	7.206	6.863
60% Ethanol	298k	$\log\beta_1$	3.505	3.486
		$\log\beta_2$	4.832	5.218
		$\log\beta_3$	7.274	6.773
	308k	$\log\beta_1$	3.477	3.455
		$\log\beta_2$	4.819	5.215
		$\log\beta_3$	7.260	6.799
60% DMSO	298k	$\log\beta_1$	3.096	2.945
		$\log\beta_2$	4.638	4.909
		$\log\beta_3$	4.909	6.696
	308k	$\log\beta_1$	3.079	3.06
		$\log\beta_2$	4.629	5,005
		$\log\beta_3$	7.193	6.773

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