RJC

http://www.rasayanjournal.com

ELECTROCHEMICAL AND THERMODYNAMIC BEHAVIOUR AT DME OF CADMIUM(II) WITH ITACONIC ACID IN NON-AQUEOUS MEDIA (20%, 40%, 60% DMSO)

Chanchal Karadia* and O.D. Gupta

Department of Chemistry, University of Rajasthan, Jaipur (Rajasthan) 302004 India
*E-mail:chanchalkaradia@rediffmail.com

ABSTRACT

Studies of Cd(II) complexes with Itaconic acid have been carried out by polarographic method in non-aqueous media (20%, 40%, 60% 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 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.

Keywords: Cd(II); Itaconic acid; Stability constants; Polarographic study; 20%, 40%, 60% DMSO (Dimethylsulphoxide)

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 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 DMF has been studied by K. Selveraj and coworkers[8]. V. Sharma[9] has reported the electrokinetic study of Gallium(III) with DL- -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 DME Polarographic study of Cd(II) with crown ethers in non-aqueous solvents have been carried out by G. Rounaghi and coworkers[11,12]. Many workers have been studied electrochemical behaviour of Co(II) in acetonitrile-water mixtures at DME[13]. K. Saini, H.P. Gupta and R.S. Pandey[14,15] have studied the complexes of Cd(II) with antibiotic drug at DME in 20% Methanol-water and Ethanol-water mixture 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 non-aqueous media (20%, 40%, 60% DMSO) in order to know the nature of the polarographic wave and the 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 a SCE as reference electrode. Constant temperature (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 0.5 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% DMSO) (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 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 $_j$ were calculated by the graphical extrapolation method. The experimentally determined values calculated for Cd(II)-Itaconic acid system in 20% DMSO media at 298K and 308K are recorded. The overall formation constants were obtained by extrapolation of $F_j[(X)]$ to the zero ligand concentration. The formation constants log b_1, log b_2 and log b_3 of the three complex species are 3.041, 4.623 and 7.161 at 298K respectively. The same values at 308K are 2.977, 4.579 and 7.158 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 are recorded at 298K and 308K. The formation constant log b_1, log b_2 and log b_3 of the three complex species formed are 3.033, 4.612 and 7.176 at 298K and the same values at 308K are 3.000, 4.596 and 7.170 respectively.

In 60% 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. The formation constant log b_1, log b_2 and log b_3 of the three complex species formed are 3.096, 4.638 and 7.220 at 298K and the same values at 308K are 3.079, 4.623 and 7.193, 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% DMSO 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% DMSO solvent mixtures

Metal complex species	log b_i		$\Delta G°(-)$	$\Delta H°(-)$	$\Delta S°(+)$
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.041	2.977	4.144	2.688	0.004
MX_2	4.623	4.579	6.301	1.848	0.014
MX_3	7.161	7.158	9.760	0.126	0.032

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 20%, 40%, 60% DMSO solvents have also been further verified by mathematical method given by Mihailov and datas are given in Table 4.

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

Metal complex species	log b_i		$\Delta G°(-)$	$\Delta H°(-)$	$\Delta S°(+)$
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.033	3.000	4.133	1.386	0.009
MX_2	4.612	4.596	6.286	0.672	0.018
MX_3	7.176	7.170	9.780	0.252	0.031

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

Metal complex species	log b_i		$\Delta G°(-)$	$\Delta H°(-)$	$\Delta S°(+)$
	298K	308K	K.cal/mole	K.cal/mole	K.cal/mole/deg.
MX_1	3.096	3.079	4.219	0.714	0.011
MX_2	4.638	4.623	6.321	0.630	0.019
MX_3	7.220	7.193	9.840	1.134	0.029

Table-4: DeFord and Hume's and Mihailov's stability constants of Cd(II)-Itaconate system in nonaqueous solvent mixture.

Solvent	Temp.	log b_i	DeFord and Hume	Mihailov
20% DMSO	298K	log b_1	3.041	2.920
		log b_2	4.623	4.974
		log b_3	7.161	6.852
	308K	log b_1	2.977	2.936
		log b_2	4.579	4.984
		log b_3	7.158	6.863
40% DMSO	298K	log b_1	3.033	2.976
		log b_2	4.612	5.032
		log b_3	7.176	6.912
	308K	log b_1	3.000	2.960
		log b_2	4.596	5.003
		log b_3	7.170	6.669
60% DMSO	298K	log b_1	3.096	2.945
		log b_2	4.638	4.909
		log b_3	7.220	6.696
	308K	log b_1	3.079	3.060
		log b_2	4.623	5.005
		log b_3	7.193	6.773

REFERENCES

1. I. M. Kolthoff and J Lingane, *J. Polarography*, **1**, 211 (1952).
2. D. D. DeFord and Hume D N, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
3. A. Baric and H. Branica, *J. Polarog. Soc.*, **13**, 4 (1967).
4. H. Billinski, S. Kozar, Z. Kwokar and M. Branica, *Thalassia Jugosi*, **13**, 101 (1977).
5. J. I. Walters and R. D. Witt, *J. Am. Chem. Soc.*, **76**, 3810 (1954).
6. B.H. Cruz, J M Diaz-Cruz, I J Sestakova, *Electroanal Chem.*, **520**, 111 (2000).
7. M. K. Verma, and C. P. S. Chandel, *Oriental J. Chem.*, **21**, (2004).
8. K. Selvaraj, J. Mallika, A. Selvaraj, *Oriental J. Chem.*, **20**, 23, 2004.
9. V. Sharma and K. D. Gupta, *Asian J. Chem.*, **16**, 1398 (2004).
10. R. K. Lohiya, P. L. Pratihar, R. V. Singh and S K. Mukherjee, *Oriental J. Chem.*, **17**, (2001).
11. G. Rounaghi and A. Sarafraz and Z Monsef, *J. Inclusion Phenomena and Macrocyclic Chemistry*, **39**, 3 (2001).
12. C. Rounaghi, Z. Eshagi and E. Ghiamat, *J. Inclusion Phenomena and Macrocylic Chemistry*, **38**, 1 (2000).
13. K. Selveraj, J. Malika and A. Selvaraj, *Oriental J. Chem.*, **20(1)**, 2003.
14. K. Saini, H.P. Gupta and Pandey R.S., *J. Indian Chem. Soc.*, **83**, 2006.
15. K. Saini, H.P. Gupta and R.S. Pandey, *Bull. Electrochem.*, **20**, 2004.

We proudly inform to all our Authors and Readers that, our journal…

RASĀYAN Journal of Chemistry

has been abstracted in
SCOPUS *(Elsevier, the Netherlands)*

It has been already abstracted (right from its first issue) in the following abstracting agencies-

- AQUATIC SCIENCE AND FISHERIES ABSTRACTS (USA)
- CAB ABSTRACTS (UK)
- CHEMICAL ABSTRACTS (USA)
- CAPLUS (USA)
- CSA ILLUMINA NATURAL SCIENCES (USA)
- GLOBAL HEALTH (UK)
- INDIAN SCIENCE ABSTRACTS (INDIA)
- MEDICINAL AND AROMATIC PLANT ABSTRACTS (INDIA)
- METEOROLOGICAL AND GEOASTROPHYSICAL ABSTRACTS (USA)
- NANOTECHNOLOGY ABSTRACTS (USA)
- POLLUTION ABSTRACTS (USA)
- RUSSIAN PERIODICALS CATALOG
- ULRICH'S PERIODICALS DIRECTORY (USA)
- WATER RESOURCES ABSTRACTS (USA)