



## NOTE

### Study of Complex Formation Between Malonic Acid and Cd(II) Ion in Aqueous and Non-Aqueous Solvents using Polarography

R.P. YADAV and O.D. GUPTA\*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

\*Corresponding author: E-mail: raj1sushila@yahoo.com

(Received: 8 March 2011;

Accepted: 30 November 2011)

AJC-10783

Studies of Cd(II) complexes with malonic acid have been carried out by polarographic method in aqueous and non-aqueous media (30 % DMSO, 30 % DMF, 30 % ethanol) under varying temperatures, at 303 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 malonic 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  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  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), Malonic acid, Stability constants, Polarographic study, Ethanol, DMF, DMSO.

The early studies done by Zanko and Manusova<sup>1</sup> using polarography in aqueous-organic solvent mixture, it has become possible to carry out various measurements for both inorganic and organic substances in nonaqueous media. The polarographic<sup>2-5</sup> study of metal complexes of Cd(II) has been widely taken. Polarographic studies on Cd(II) with some bicarboxylic acid have been carried out by many workers<sup>6</sup>. Electrochemical behaviour of Co(II) in acetonitrile-water mixtures at DME has been studied by Selveraj and coworkers<sup>7</sup>. Sharma<sup>8</sup> has reported the electrokinetic study of gallium(III) with DL- $\alpha$ -alanine in aqueous and 25 % ethanol at d.m.e. Many workers<sup>9</sup> have been studied the copper complexes in aqueous and non-aqueous (DMF, CH<sub>3</sub>CN) media at d.m.e. polarographic study of Cd(II) with crown ethers in non-aqueous solvents have been carried out by Rounaghi and coworkers<sup>10,11</sup>. Many workers<sup>12</sup> have been studied electrochemical behaviour of Co(II) in acetonitrile-water mixtures at DME. Saini, Gupta and Pandey *et al.*<sup>13,14</sup> 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 malonic acid did not receive much attention. A detailed study of electrochemical behaviour of malonic acid in aqueous and non-aqueous media (30 % DMSO, 30 % DMF, 30 % ethanol) in order to know the nature of the polarographic wave and the stability of metal complexes by changing polarity of the solvent.

A.R. grade chemicals were used. Cadmium(II) nitrate was used in this study. The capillary characteristics are  $m = 1.75$  mg/s and  $t = 3.8$  s. The potentials were measured against a SCE as reference electrode. Constant temperatures (303 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 0.1 mM Cd(II) and various concentrations of malonic acid and requisite amount of supporting electrolyte were prepared. Solutions were deaerated with nitrogen gas before analysis.

The reduction of Cd(II) in presence of malonic acid was found to be reversible in non-aqueous media (30 % DMSO, 30 % DMF, 30 % ethanol) (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 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.

In 30 % DMF (v/v) solvent the overall formation constant  $\log \beta_1$ ,  $\log \beta_2$  and  $\log \beta_3$  of the three complex species formed are 1.69, 2.73 and 3.47 at 303 K and the same values at 308 K are 1.67, 2.72 and 3.45, respectively.

In 30 % ethanol (v/v) solvent the overall formation constant for Cd(II) malonic acid system were also calculated by graphical method of DeFord and Hume. The values of polarographic parameters are recorded at 303 and 308 K. The formation constant  $\log \beta_1$ ,  $\log \beta_2$  and  $\log \beta_3$  of the three complex species formed are 1.63, 2.69 and 3.35 at 303 K and the same values at 308 K are 1.67, 2.73 and 3.45 respectively.

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

The overall change in thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  on complex formation for Cd(II) with malonic acid system in 30 % DMSO, 30 % DMF and 30 % ethanol media are recorded in Tables 1-3, respectively.

TABLE-1  
STABILITY CONSTANTS AND THERMODYNAMIC  
PARAMETERS OF Cd(II) MALONIC ACID SYSTEM IN  
30 % DMSO SOLVENT MIXTURE

Metal complex species	$\log \beta_j$		$-\Delta G^\circ$ (Kcal/mol)	$-\Delta H^\circ$ (Kcal/mol)	$\Delta S^\circ$ (Kcal/mol/deg)
	303 K	308 K			
$MX_1$	1.69	1.67	2.355	1.902	1.495
$MX_2$	2.73	2.72	3.788	0.874	11.60
$MX_3$	3.47	3.45	4.809	1.645	10.49

TABLE-2  
STABILITY CONSTANTS AND THERMODYNAMIC  
PARAMETERS OF Cd(II) MALONIC ACID SYSTEM  
IN 30% DMF SOLVENT MIXTURE

Metal complex species	$\log \beta_j$		$-\Delta G^\circ$ (Kcal/mol)	$-\Delta H^\circ$ (Kcal/mol)	$\Delta S^\circ$ (Kcal/mol/deg)
	303 K	308 K			
$MX_1$	1.68	1.65	2.330	2.390	-0.207
$MX_2$	2.71	2.70	3.756	4.370	+10.930
$MX_3$	3.41	3.38	4.726	2.239	+8.200

TABLE-3  
STABILITY CONSTANTS AND THERMODYNAMIC  
PARAMETERS OF Cd(II) MALONIC ACID SYSTEM  
IN 30 % ETHANOL SOLVENT MIXTURE

Metal complex species	$\log \beta_j$		$-\Delta G^\circ$ (Kcal/mol)	$-\Delta H^\circ$ (Kcal/mol)	$\Delta S^\circ$ (Kcal/mol/deg)
	303 K	308 K			
$MX_1$	1.63	1.67	2.271	2.195	0.2518
$MX_2$	2.69	2.73	3.738	0.299	11.355
$MX_3$	3.35	3.45	4.673	1.448	10.645

The more negative value of  $\Delta G^\circ$  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  $\Delta H^\circ$  suggest that the formation of these complexes is an exothermic process.

The values of stability constants for Cd(II) malonic acid system in 30 % DMSO, 30 % DMF and 30 % ethanol solvent have also been further verified by mathematical method given by Mihailov and data are given in Table-4.

TABLE-4  
DEFORD AND HUME'S AND MIHAILOV'S STABILITY  
CONSTANTS OF Cd(II) MALONIC ACID SYSTEM

Solvent	Temp.	$\log \beta_j$	DeFord and Hume	Mihailov
30 % DMSO	303 K	$\log \beta_1$	1.69	1.67
		$\log \beta_2$	2.73	2.76
		$\log \beta_3$	3.47	3.66
	308 K	$\log \beta_1$	1.67	1.66
		$\log \beta_2$	2.72	2.83
		$\log \beta_3$	3.45	3.96
30% DMF	303 K	$\log \beta_1$	1.68	1.7
		$\log \beta_2$	2.71	2.74
		$\log \beta_3$	3.41	3.62
	308 K	$\log \beta_1$	1.65	1.62
		$\log \beta_2$	2.70	2.79
		$\log \beta_3$	3.38	3.78
30% ethanol	303 K	$\log \beta_1$	1.63	1.63
		$\log \beta_2$	2.69	2.72
		$\log \beta_3$	3.35	3.63
	308 K	$\log \beta_1$	1.67	1.66
		$\log \beta_2$	2.73	2.83
		$\log \beta_3$	3.45	3.96

#### ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing facilities to carry out this research.

#### REFERENCES

1. A.M. Zanko and F.A. Manusova, *Zh. Obshch. Khim.*, **10**, 1171 (1940).
2. A. Baric and H. Branica, *J. Polarog. Soc.*, **13**, 4 (1967).
3. H. Billinski, S. Kozar, Z. Kwokar and M. Branica, *Thalassia. Jugosi.*, **13**, 101 (1977).
4. J.I. Walters and R.D. Witt, *J. Am. Chem. Soc.*, **76**, 3810 (1954).
5. B.H. Cruz, J.M. Diaz-Cruz and I.J. Sestakova, *Electroanal. Chem.*, **520**, 111 (2000).
6. M.K. Verma and C.P.S. Chandel, *Orient. J. Chem.*, **21**, 9 (2005).
7. K. Selvaraj, J. Mallika and A. Selvaraj, *Orient. J. Chem.*, **20**, 23 (2004).
8. V. Sharma and K.D. Gupta, *Asian J. Chem.*, **16**, 1398 (2004).
9. R.K. Lohiya, P.L. Pratihari, R.V. Singh and S.K. Mukherjee, *Orient. J. Chem.*, **17**, (2001).
10. G. Rounaghi, A. Sarafraz and Z. Monsef, *J. Incl. Phenom. Macrocycl. Chem.*, **39**, 3 (2001).
11. C. Rounaghi, Z. Eshagi and E. Ghiamat, *J. Incl. Phenom. Macrocycl. Chem.*, **38**, 1 (2000).
12. K. Selvaraj, J. Mallika and A. Selvaraj, *Orient. J. Chem.*, **20**, 23 (2003).
13. K. Saini, H.P. Gupta and R.S. Pandey, *J. Indian Chem. Soc.*, **83**, 495 (2006).
14. K. Saini, H.P. Gupta and R.S. Pandey, *Bull. Electrochem.*, **20**, 487 (2004).