Thermodynamics of Complex Formation : Cadmium Malonate System

S. S. KELKAR AND B. I. NEMADE*

*Department of Chemistry, University of Bombay, Vidyanagari, Santacrus (E), Bombay-400 098.

MALONATE complexes of cadmium were studied polarographically at three different temperatures, viz. 30, 40 and 50°C. The overall stability constants were evaluated by DeFord and Hume's method. The value found are log β=2.00, 2.04, 2.08, log β_2=2.78, 3.04, 3.23 and log β_3=3.43, 3.68, 3.81 at 30, 40 and 50°C respectively. The stability constants obtained at various temperatures were used to calculate various thermodynamic functions by graphical method.

CADMIUM-MALONATE system has been studied polarographically by workers[1-3]. However less attention was paid towards the thermodynamics of complex formation which has potentiality to provide good insight about complexation phenomenon,

Hence studies of cadium-malonate complexes at different temperature were undertaken in order to have berter understanding of the effect of temperatures on such systems.

EXPERIMENTAL

A balancing type[4] manual polarograph was set up to obtain current-potential curves. The saturated calomel electrode (SCE) was used as the reference electrode. All polarographic measurements were carried out in a water thermostat (Accuracy ±.1°C). pH of the test solutions was maintained at 7.00±.1 All the chemicals used were AR grade. Sodium perchlorate was used as the suppoiting electrolyte and ionic strength was maintained at 2.0. No maxima suppresser was found necessary.

The capillary characteristics were m=1.98mg/sec t=3.6 sec, in the supporting electrolyte, in open circuit.

RESULTS AND DISCUSSION

A well-defined single wave was obtained for cadium in 2.0 M sodium perchlorate at 30, 40 and 50°C in presence and absence of complexing agent. The diffusion current increased with the increase in temperature and the temperature coefficient of diffusion current, calculated by method of Maites[5], gave a value of about 1.4 percent per degree, which indicated diffusion controlled nature of reduction. The half-wave potential for the simple ion was shifted to more positive values with the increase in temperature as observed by other workers[6].

The dissociation constant (pK_2) of the malonic acid under the present experimental conditions was not available and hence determined by the technique illustrated by Irving and Rossetti[7].

A value of 5.00 for pK_2, obtained by this procedure was used in the present investigation. The temperature coefficient of the dissociation constant[8] was found to be negligible in the temperature range 30 to 50°C and hence the same value was taken for all the temperature. The free ligand-malonate ion concentration-(A)-was calculated by the formula.

$$A = a/[(1 + \text{antilog}\ (pK_2 - pH)] \qquad (1)$$

Where 'a' is the analytical concentration of the acid. The experiments were conducted at pH of 7 where malonic acid would exist as malonate ion.

Polarograms of cadmium were recorded at different concentrations of malonic acid. The slopes of Log-plots indicated reversible reduction. The half-wave potantials, measured as a function of ligand concentration at 30, 40 and 50°C are represented in Table 1. The plots of $\Delta E_{\frac{1}{2}}$ vs pA (-log A) resulted in the smooth curves in all the three cases (Fig. 1) indicating the presence of different species whose stabilities do not differ appreciably. As the method of Lingane[9] could not be adopted in such cases, method developed by DeFord and Hume[10] was used for the evaluation of successive formation constants The function F_0 (A) was calculated from the shift in the half-wave potential obtained from the smooth curve of a plot of $E_{\frac{1}{2}}$ vs pA and was analysed by graphical method, Three complexes were observed at all the three temperatures; The values of overall stability constants are presented in Table 2.

TABLE 1

$E_{\frac{1}{2}}$ vs. pA — Effect of Temperature

Cd = 0.4 mM ; μ = 2.0 ; pH = 7.0 ± 0.1 $m^{2/3} + {}^{1}/_{6} = 1.95\ mg^{2/3}\ sec.^{-1/2}$;

H A	pA	Temperature					
		30°C		40°C		50°C	
		$E_{\frac{1}{2}}$ — V vs. S.C.E.	i_d μA	$E_{\frac{1}{2}}$ —V vs. S.C.E.	i_d μA	$E_{\frac{1}{2}}$ —V vs. S.C.E.	i_d μA
0.00	—	0.558	2.82	0.552	3.18	0.543	3.65
0.02	1.70	0.575	2.67	0.569	3.02	0.560	3.35
0.04	1.40	0.583	2.55	0.579	2.80	0.574	3.24
0.07	1.15	0.589	2 45	0.588	2.76	0.582	3.15
0.10	1.00	0.597	2.40	0.595	2.75	0.593	3.07
0.15	0.82	0.604	2.31	0,605	2.73	0.603	3.07
0.20	0.70	0.609	2.30	0.616	2.61	0.608	2.93
0.25	0.60	0.615	2.23	0.621	2.57	0.616	2.90
0.30	0.52	0.621	2.22	0 624	2.57	0.621	2.91
0.35	0.46	0.625	2.17	0.627	2.53	0.628	2.90
0.40	0.40	0.631	2.19	0.632	2.49	0.631	2.84
0.50	0.30	0.637	2.12	0.640	2.43	0.639	2.85

TABLE 2

Stability constants and thermodyamic functions

Ccmplex	10g β_J^T			− ΔF° K Cal/mole		ΔH° K. Cal/ mole	ΔS° Cal/ deg./mole
	30°C	40°C	50°C	40°C	50°C		
Cd (Mal)	2.00	2.04	2.08	2.9	3.1	1.05	12.9
Cd $(Mal)_2$	2.78	3.04	3.23	4.4	4.8	9.6	42.3
Cd $(Mal)_3$	3.43	3.68	3.81	5.3	5.7	8.0	42.3

The stability constants are directly related to free energy change accompanying the complex formation through a simple relation

$$\Delta F^\circ = -RT \text{ in } K \qquad (2)$$

Where K is the equilibrium constant. The change in the free energy can be resolved in the enthalpy and entropy terms with the help of following equation.

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (3)$$

Combining eq (2) and (3), we can write

$$-RT\ 1nk = \Delta H^\circ - T\Delta S^\circ$$

$$\log K = -\frac{\Delta H^\circ}{2.303\ R}\frac{1}{T} + \frac{\Delta S^\circ}{2.303\ R} \qquad (5)$$

At a comparatively narrow range of temperature the value of ΔH° and ΔS° can be taken to be constant. Hence the plot of log K vs (1/T) results in to a straight line whose slope equals to $-\Delta H^\circ/2.303\ R$ and intercept gives $\Delta S^\circ/2.303\ R$.

The accuracy of the values of the above function determined by the temperature coefficient method depends upon the accurate determination of stability constants. Many workers have used the stability constants obtained by the polarographic

technique to evaluate the thermodynamic function by the above method[11,12].

FIG 1 $\Delta E_{1/2}$ vs. pA

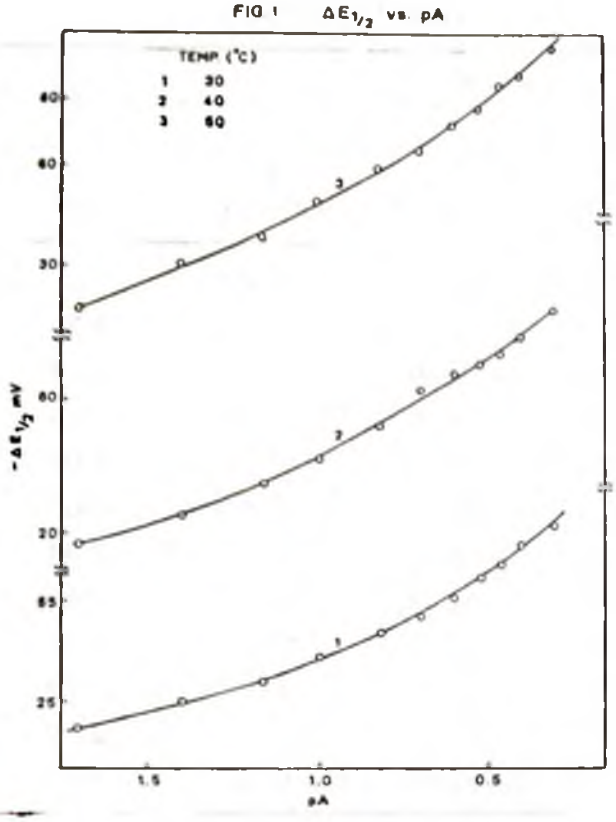
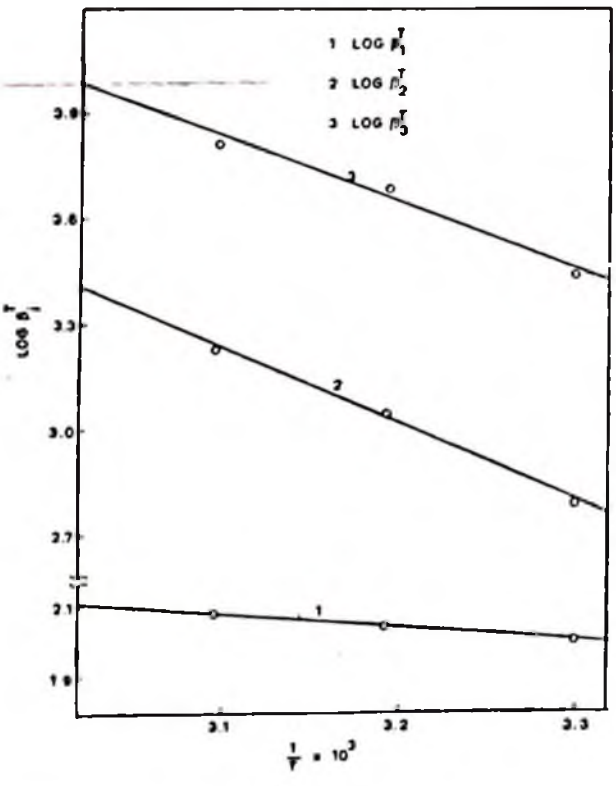


FIG. 2. PLOT OF β_i^T vs. 1/T



The plot of log β_j^T vs 1/T. where 'T' is the absolute temperature, is given in Fig 2. The values of the various parameters, viz ΔF°, ΔN° and ΔS° are given in Table 2.

The stability of complex changes with the change n temperature, depending upon the thermodynamics of complexation reaction. For the reactions which are exothermic in nature the stability of of complex decreases with the increase in temperature and enhances for the endothermic reactions. The stability of complexes was found to enhance by an increase in temperature (Table 2) showing the endothermic nature of reaction which seems to be the general tendency of dicarboxylic acid complexes.[13]

Acknowledgement

The authors wish to express their thanks to Dr. A.K. Sundaram and Dr. R. Sundaresan at Analytical Chemistry Division, B.A.R.C., Bombay for the valuable discussion and helpful suggestions.

REFERENCES

1. J. N. Gaur and M. M. Palrecha, *J. Polarogr Soc.*, 14 (1968) 31.
2. T. Nozaki, M. Kadowski, D. Sagawa and K. Orita, *Nippon Kagaku Zasshi*, 91 (1970) 64.
3. A.K. Maheshwari, D.S. Jain, H.C. Saraswat and J.N. Gaur, *Proc, XIV Seminar Electrochem.*, Karaikudi (1973) 345.
4. I. M, Kolthoff and J. J. Lingane, *Polarography* Interscience Publishers, New York, (1946), Vol-1, P. 49.
5. L. Meitess, *Polarographic Techniques*, Interscience Publishers, Inc, New York, 1965.
6. R. S. Saxena and U. S. Chaturvedi, *J. Ind. Chem. Soc.*, 49 (1972) 521
7. M. Irving and H.S. Rossotti, *J. Chem. Soc.*, (1954) 290.
8. R. A. Robinson and R. H. Stokes, *Electrolyte solutions*, Butterworths & Co. Ltd., London (1970) APP 12.1
9. J. J. Lingane, *Chem. Revs.*, 29 (1941) 1.
10. D. DeFord and H. N. Hume, *J. Am. Chem. Soc.*, 73 (1941) 5321.
11. J. K. Gupta and C. M. Gupta, *Ind. J. Chem.*, 6 (1968) 50.
12. B. S. Pannu and S. L. Chopra, *J. Ind. Chem. Soc.*, 9 (1973) 629.
13. S. J. Ashcroft and C. T. Mortimer, *Thermochemistry of Transition Metal Complexes*, Academic Press, London (1970) 88.