

Polarographic Studies and Thermodynamic Behaviour of Cd(II) Complexes with Thiophene-2-acetate

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Polarographic studies and thermodynamic behaviour of Cd(II) complexes with thiophene-2-acetate have been studied. In this system cadmium(II) reduces reversibly with the involvement of two electrons, as the slopes of plots of $\log \frac{i}{i_d - i}$ vs. $E_{d.e.}$ varied within 31 ± 2 mV. The diffusion controlled nature of reduction was revealed from the straight line plots of i_d vs. $\sqrt{h_{eff}}$. The overall formation constants were determined by DeFord method. It was found that there was no change in the number of species formed by increasing the temperature from 30 to 40°C but the stability constants of the complexes decreased with rise in temperature. The negative enthalpy change in Cd-thiophene-2-acetate also confirmed the complex formation.

INTRODUCTION

The nature of the reduction at the dropping mercury electrode of divalent metal ions complexed with aliphatic organic acids has been investigated¹⁻⁶. From the survey of the literature, it appears that little attention has been paid to the polarographic studies of the complexes formed by divalent metal ions with heterocyclic ligands. The studies of complexes of cadmium and zinc with pyridine and its substituted compounds have been carried out for the reduction of the complexes formed by divalent metal ions with heterocyclic ligands containing oxygen as hetero atom at dropping mercury electrode.

Indium and cadmium are suitable metal ions for polarography, because they possess favourable polarographic characteristics and can be determined in a variety of supporting electrolytes. The reduction of indium, lead and cadmium has been studied in various complexing and non-complexing media,⁷⁻¹⁵ which reveals that indium(III) reduces reversibly as well as quasi-reversibly. The overall formation constants of various complex species formed in aqueous solutions have been evaluated by DeFord and Hume's method.¹⁶ Lingane's method¹⁷ has also been applied where only one complex species is present. Apart from this, the overall formation constants of some complexes have been calculated by Mikhailov's mathematical method¹⁸. Thermodynamics and relative distribution of complexes and uncomplexed metal ions in the solution have also been discussed. The present studies deal with the determination of composition and formation constants of the complexes formed by Cd²⁺ with thiophene-2-acetate.

EXPERIMENTAL

All reagents used were of analytical grade. The solutions were prepared in

conductivity water. The solution of cadmium(II) was prepared by dissolving the weighed amount of cadmium nitrate in conductivity water. The solutions were standardised by usual methods. Sodium salt of thiophene 2-acetic acid was used as complexing agent. The supporting electrolytes used were KNO_3 and NaClO_4 and their requisite quantity maintained the ionic strength. Constant pH of all the solutions was controlled at 6.7–6.8. 0.005% Gelatin was used as maxima suppressor. Polarograms were obtained from test solutions kept in thermostat H-cell with a saturated calomel electrode. Prior to the polarographic examination of each solution, purified nitrogen was passed through it for about 25 minutes to expel dissolved oxygen. A gradual increase in applied potential resulted in variation in current as observed on damped spot galvanometer (Ajco, model No. P-GI, Sr. No. P71049). The current-voltage curves were recorded.

A manual set up was used for taking polarograms. The temperature was controlled by a Haake type thermostat. The dropping mercury electrode used had the following characteristics: $m = 1.9$ mg per sec and $t = 3.5$ sec in open circuit. Height of the mercury column was 50 cm.

RESULTS AND DISCUSSION

In presence of thiophene-2-acetate ions Cd^{2+} ions produce single well defined reduction wave. As a result of complex formation, the diffusion current decreases due to large size of complex ion formed in comparison to the aquo metal ion, and half wave potential shifts to more negative value with increasing ligand concentration.

The system is diffusion controlled as the plots of i_d vs. C (C stands for metal ion concentration) and i_d vs. $\sqrt{h_{\text{eff}}}$ (where h is effective height of mercury column) were found to be linear passing through origin. The plots of $\log \frac{i}{i_d - i}$ vs. $E_{d.e.}$ were found to be linear with a slope 31 ± 2 mV showing the reversible nature of reduction. The plots of $E_{1/2}$ vs. $\log C_x$ were found to be smooth as shown in Fig. 1a indicating that two or more complex species are formed.

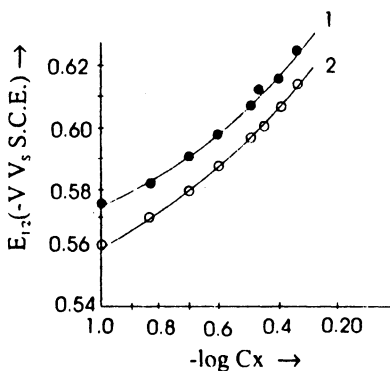


Fig. 1a. Plots of $E_{1/2}$ vs. $\log C_x$
 (1) Cd^{2+} -Thiophene-2-acetate system at 30°C
 (2) Cd^{2+} -Thiophene-2-acetate system at 40°C

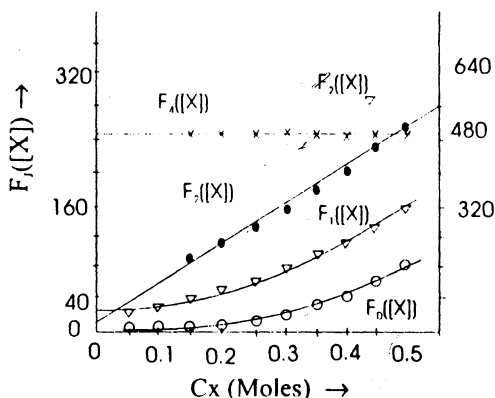


Fig. 1b. Plots of $F_j([X])$ vs. $\log C_x$ Cd^{2+} -Thiophene-2-acetate system at 30°C

The number of species were analysed by applying the modified DeFord and Hume's treatment¹⁶ by plotting the $F_j([X])$ functions vs. C_x . In case of Cd^{2+} thiophene-2-acetate system, the plot of $F_0([X])$ and $F_1([X])$ vs. C_x were smooth curves confirming the existence of two or more complex species in equilibrium. The plot of $F_2([X])$ vs. C_x was a straight line with a slope, the intercept of which gives the value of β_2 and plot of $F_3([X])$ vs. C_x comes out to be a straight line parallel to C_x axis (Fig.1b) showing the existence of three complex species of cadmium with thiophene-2-acetate ion having the composition $[\text{Cd}(\text{Thiophene-2-acetate})]^+$, $[\text{Cd}(\text{Thiophene-2-acetate})_2]^-$ and $[\text{Cd}(\text{Thiophene-2-acetate})_3]^{-1}$. The polarographic characteristics and $F_j([X])$ function at 30°C for the system are summarised in Table-1.

The experiments were repeated for Cd-thiophene-2-acetate system at 40°C under identical conditions. The $F_j([X])$ functions are summarised in Table-2. The number of species at 40°C also remains the same as were at 30°C (Fig. 1c). The values of overall formation constants for Cd-thiophene-2-acetate system at 30°C and 40°C are given below.

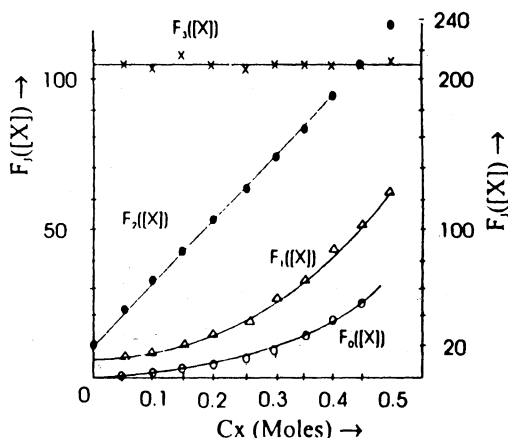


Fig. 1c. Plots of $F_j([X])$ vs. $\log C_x$ for Cd^{2+} -Thiophene-2-acetate system at 40°C

Cd-THIOPHENE-2-ACETATE SYSTEM AT IONIC STRENGTH 1.5

Temperature (°C)	Overall formation constants		
	β_1	β_2	β_3
30	29	14	490
40	6	11	210

TABLE-1
POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR CADMIUM-THIOPHENE-2-ACETATE SYSTEM AT 30°C

$Cd^{2+} = 1.0 \text{ mM}$; $\mu = 1.5 \text{ M (NaClO}_4\text{)}$; $pH = 6.2 \pm 1$

Cx (mol)	$E_{1/2}$ (-V vs. S.C.E.)	i_d (divs.)	$F_0([X])$	$F_1([X])$	$F_2([X])$	$F_3([X])$
0.00	0.5520	100.5	-	-	-	-
0.05	0.5610	65.5	2.3	26.0	-	-
0.10	0.5750	64.5	3.5	25.0	-	-
0.15	0.5810	49.5	7.3	42.0	87.2	488
0.20	0.5910	55.5	11.2	51.4	112.4	492
0.25	0.5980	48.5	16.7	63.1	136.7	491
0.30	0.6070	47.5	24.3	77.7	162.5	495
0.35	0.6120	47.0	33.8	93.9	185.5	490
0.40	0.6160	47.0	45.4	111.2	205.6	479
0.45	0.6230	42.5	61.1	133.7	232.7	486

TABLE-2
POLAROGRAPHIC CHARACTERISTICS AND $F_j([X])$ FUNCTIONS FOR CADMIUM-THIOPHENE-2-ACETATE SYSTEM AT 40°C

$Cd^{2+} = 1.0 \text{ mM}$; $\mu = 1.5 \text{ M (NaClO}_4\text{)}$; $pH = 6.2 \pm 1$

Cx (mol)	$E_{1/2}$ (-V vs. S.C. E.)	i_d (divs.)	$F_0([X])$	$F_1([X])$	$F_2([X])$	$F_3([X])$
0.00	0.5480	106.0	-	-	-	-
0.05	0.5560	107.0	1,354	7.08	21.60	212
0.10	0.5580	110.0	1,918	9.18	31.80	208
0.15	0.5710	100.0	2,885	12.57	43.85	219
0.20	0.5800	98.0	4,320	16.60	53.00	210
0.25	0.5880	98.0	6,420	21.68	62.75	207
0.30	0.5970	94.5	9,433	28.11	73.70	209
0.35	0.6002	95.0	13,365	35.33	83.80	208
0.40	0.6075	91.0	18,664	44.16	95.40	211
0.45	0.6125	86.5	25,246	53.88	106.40	212
0.50	0.6158	86.0	33,500	65.00	118.00	214

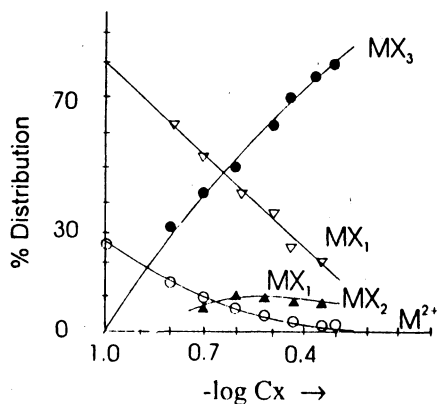


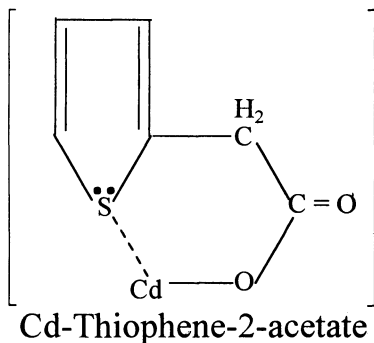
Fig. 1d Relative distribution Cd^{2+} -Thiophene-2-acetate system at 30°C

The distributions of various species for Cd^{2+} as a logarithmic function of ligand concentration are presented in Fig. 1d. The effect of temperature on half wave potential is often used to establish the reversibility of electrode reaction and also helps to evaluate the thermodynamic parameters for the reaction equilibria from the following relationship:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

Complex species	ΔG° kcal mol ⁻¹	ΔH° kcal mol ⁻¹	ΔS° kcal mol ⁻¹ deg ⁻¹
$\text{Cd}(\text{X})_3$	-3.391	-13.26	-40.77

In the case of thiophene-2-acetate system, the delocalisation makes the electron less available on hetero sulphur atom thus making the tendency of hetero sulphur atom less towards donating. This shows that the hetero-sulphur atom also donates electrons to the metal ion. The proposed structure may be written as:



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