Electrochemical Behaviour of the Complexes of Cd(II), Pb(II) and Cu(II) in the presence of Citraconate Ions at Dropping Mercury Electrode

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POLAROGRAPHIC behaviour of the title complexes is studied. Reduction was found to be diffusion controlled in all the cases. Both Cd(II) and Pb(II) form three complexes MX_1, MX_2 and MX_3 whereas Cu(II) forms four complexes MX_1, MX_2, MX_3 and MX_4. The formation constants of the complexes formed have been calculated by DeFord and Hume's method as modified by Irving. The complexes formed by Cu(II) are much stronger than those of Pb(II) and Cd(II). The complexes of Cd(II) and Pb(II) have been studied at 30°C and 40°C and the thermodynamic functions have been calculated.

THERE are many publications[1] on the stability of complexes formed by metal ions with dibasic acids. Palrecha[2-4] has studied the complexes of malonate, succinate, glutarate and adipate ions polarographically. Maheshwari[5-6] has reported the polarographic study of malonic acid complexes and Sharma[7] has reported the electrochemical study of the melate and fumerate ions with metals. However, little attention has been paid to the electrochemical behaviour of unsaturated dicarboxylic acids.

The present work comprises the polarographic investigations on the interaction of citraconate ions with Cd(II), Pb(II) and Cu(II).

EXPERIMENTAL

All the chemicals used were of reagent grade. Stock solutions (M/40) of the metal ions were prepared by dissolving their nitrates in double distilled water. Sodium salt of citraconic acid was used as the complexing agent. Various solutions prepared contained 1.0 mM of the metal ion with varying concentrations of the ligand. The ionic strength was kept constant (at $\mu = 1.5$) by adding requisite amounts of sodium per chlorate. Triton × 100 (.001% in final solution) was used to suppress the maximum in the case of simple metal ion only, in the case of (II) system. However, no maximum appeared in the presence of the ligand. The pH of the solutions was measured to be 6.4 ± .1 by a Toshniwal mains operated pH meter.

A manual polarographic set up with W. G. Pye galvanometer was used to obtained the current-voltage curves. The dropping mercury electrode having the following characteristics $m = 1.7645$ mg/sec. and $t = 3.64$ sec. (open circuit) was used. The measurements were carried out at constant temperatures (30° and 40°C) for Cd(II) and Pb(II) and at 30°C only for Cu(II).

The temperature was maintained by Haake type ultra thermostant. H-type cell with agar-agar plug saturated with sodium chloride was used as the electrolytic vessel. The polarograms were recorded after deaeration with purified nitrogen for 20-25 minutes. The measurements refer to the SCE. as the non-polarisable electrode.

RESULTS AND DISCUSSION

A single well defined reduction wave appeared in each case. Plots of i_d vs $\sqrt{h}$ and i_d vs C_M (C_M is metal ion concentration) are linear and pass through the origin. The plots of log $[i/i_d - i]$ E_{dme} vs are linear with a slope of the order of 32 ± 3 mV. The above results showed that the electrode process is diffusion controlled and reversible two electron reduction process. The decrease in diffusion current and the shift in $E_{1/2}$ indicates the formation of citraconate complexes of Cd(II), Pb(II) and Cu(II). The plots of $E_{\frac{1}{2}}$ vs-log C_L (C_L = citraconate ion concentration) were smooth curves showing the formation of two or more complexes in equilibrium.

The value of 'p' from the limiting slope has been found to be three for Cd (II) and Pb (II) systems and four for the Cu (II) system. However Lingane's[8] method could not be applied and so the DeFord and Hume's method as modified by Irving[9] has been applied to calculate the composition and formation constants. Cd(II) forms three complexes ; [Cd (Citraconate)], [Cd (Citraconate)$_2$]$^{2-}$ and [Cd (Citraconate)]$^{4-}$ with $\beta_1 = 17.5$, $\beta_2 = 30.0$ and $\beta_3 = 525.0$ at 30°C and $\beta_1 = 10.0$,

$\beta_2 = 35.0$ and $\beta_3 = 1000.00$ at 40°C. Pb(II) also forms three complexes : [Pb (Citraconate)], [Pb (Citraconate)$_2$]$^{2-}$ and [Pb (Citraconate)$_3$]$^{4-}$ with $\beta_1 = 90.0$, $\beta_2 = 100.00$ and $\beta_3 = 4900$ at 30°C and $\beta_1 = 110$, $\beta_2 = 200.0$ and $\beta_3 = 5000$ at 40°C whereas Cu(II) forms four complexes : [Cu (Citraconate)], [Cu (Citraconate)$_2$]$^{2-}$, [Cu (Citraconate)$_3$]$^{4-}$ and [Cu (Citraconate)$_4$]$^{6-}$ with $\beta_1 = 150$, $\beta_2 = 1800$, $\beta_3 = 2200$ and $\beta_4 = 22000$ at 30°C.

The polarographic characteristics and F_i [(X)] values are presented in Tables I, II and III.

TABLE I

Polarographic characteristics and F_i ([X]) values of Cd (II)—citraconate systems

Cd (II) — 1.0 mM μ = 1.5

Cx (Moles)	30 C			40 C		
	i_d (divs.)	$E_{\frac{1}{2}}$ (—V vs SCE)	F ([X])	id (divs.)	$E_{\frac{1}{2}}$ (—V vs SCE)	F ([X])
0.00	81.5	0.5730	—	99.0	0.5655	—
0.10	75.0	0.4885	3.57	91.0	0.5845	4.46
0.15	73.0	0.5955	6.28	90.5	0.5900	6.75
0.20	72.5	0 6015	10 02	89.0	0.5970	11.54
0.25	72.0	0.6070	15 39	87.0	0.6045	20.54
0.30	71.0	0.6120	22 91	87.0	0 6110	34.57
0.35	69.0	0.6165	33.30	84.0	0 6170	50.01

TABLE II

Polarographic characteristics and F_i [(X)] values of Pb(II)—citraconate system

Pb (II) = 1.0mM μ = 1,5

Cx (Moles)	30°C			40°C		
	i_d (divs.)	$E_{\frac{1}{2}}$ (—V vs SCE)	F_i ([X])	i_d (divs)	$E_{\frac{1}{2}}$ (—V vs SCE)	F_n ([X])
0.00	71.0	0.3860	—	86.5	0.3830	—
0.10	69.0	0.4260	22.17	83.0	0.4250	23.59
0.15	69.0	0.4315	33.82	83.0	0.4325	41.17
0.20	69.0	0.4385	57.86	83.0	0.4390	66.73
0.25	68.0	0.4460	101.40	82.0	0.4465	117.90
0.30	66.5	0.4520	169.20	78.5	0.4530	199.60
0.35	65.5	0.4575	262.00	78.5	0.4580	300.30

The thermodynamic stability constants are related to other properties in the following manner:

$$\Delta F = 2.303\ RT \log (\beta_j)_T$$

$$\Delta H = 2.303\ RT_1T_2\ (\log \beta_{T1} - \log \beta_{T2}/(T_2 - T_1)$$

and $\Delta F = H - T\Delta S$

where ΔF is the free energy change, ΔH is the enthalphy change and ΔS is the entropy change. β_j is the formation constant of the Jth order and β_{T1} and β_{T2} are the formation constants at temperatures T_1 and T_2 respectively. The values of

TABLE III

Polarographic characteristics and F_i ([X]) values of Cu (II)—citraconate system at 30°C

Cu (II) = 1.0 mM μ = 1.5

C_x (Moles)	i_d (Divs)	$-E_{\frac{1}{2}}$ (—V vs SCE)	F_0([X]) x10^{-1}	F_1 ([X]) x10^{-1}	F_2 ([X]) x10^{-2}	F_3 ([X]) x10^{-2}	F_4 ([X]) x10^{-2}
0.00	66 0	—0.0220	—	—	—	—	—
0.10	64.0	0.0255	3.950	38.50	—	—	—
0.15	62.0	0 0335	7.539	49.59	—	—	—
0.20	62.0	0.0420	14.470	71.85	28.42	—	—
0.25	61.0	0.0500	27.170	103.20	37.28	77.12	220.5
0.30	61.0	0.0565	44.750	148.60	44.61	87.70	219.0
0.35	60.0	0.0620	69.400	198.00	52.26	97.90	216.8
0.40	60.0	0.0670	105.900	264.50	62.37	110.90	223.3
0.45	59.0	0.0720	152.100	337.80	71.73	119.40	216.4
0.50	59.0	0.0780	241.100	484.00	93.80	151.60	259.2

TABLE IV

Thermodynamic functions of complexes of Citraconate ions with Cd (II) and Pb (II)

Complex and its composition	Formation Constant 30°C	40°C	△F (K. Cals/mole)	△H (K Cals/mole)	△S (Cals/deg. mole)
Cd (II)—citraconate (1 : 3)	525	1000	—4.256	11.907	52.1
Pb (II)—citraconate (1 . 3)	4900	5000	—5.247	0.949	19.9

thermodynamic parameters are presented in Table IV.

It has been observed that in the cases of Cd (II) and Pb (II) complexes the value of β_1 increases with temperature because △H it is positive.

On comparing the values of the stabliity constants of the highest complex MX_j it can be concluded that the number of complexes and their stability is greater for the Cu (II)-citraconate system than in the cases of Pb (II) and Cd (II). Since these reduction processes are diffusion controlled, these metal ions i.e., Cd (II), Pb (II) and Cu (II) can be estimated polarographically in the presence of citraconate ions.

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