Reduction of cadmium(II) in presence of mixed ligands at D.M.E.*

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Abstract

Polarographic analysis of the electrode behaviour of cadmium(II)-malonate-thiocyanate and cadmium(II) succinate,thiocyanate systems have been made in aqueous medium at 25 ± 0·1° C. Two mixed complexes $[Cd\ (MAL)\ (SCN)]^-$ and $[Cd\ (MAL)_2\ (SCN)]^{3-}$ and $[Cd\ (SUCC)\ (SCN)]^-$ and $[Cd\ (SUCC)\ (SCN)]^{3-}$ were observed in both the systems, where MAL = malonate, SCN = thiocyanate and SUCC = succinate ions. Their log stability constants came out to be 3·08, 3·57 and 2·91, 2·50 respectively. These complexes were found to undergo reversible reduction at d.m.e. in the presence of 3·0 M ionic strength and 6·6 pH. The negative values of the stability constants for $[Cd\ (MAL)\ (SCN)_2]^{2-}$ and $[Cd\ (SUCC)\ (SCN)_2]^{2-}$ indicate the absence of these species. It is observed that the mixed ligand complexes have higher stabilities than would be predicted on statistical considerations. The observed enhancements of the complexation constant of the mixed complex species were attributed to the possibilities of (i) some weak bonding between unlike bound ligands and (ii) the gross statistical effects.

Key words : Thiocyanate, malonate, succinate, Faraday number, constant, absolute temperature, diffusion current constant.

1. Introduction

In recent years the polarographic technique is receiving considerable attention in the field of mixed ligand complexes after the work of Schaap and McMasters.[1] Mixed ligand complexes of cadmium (II) with (i) oxalate-salicylate,[2] (ii) oxalate-thiocyanate,[3] (iii) thiourea-formate,[4] (iv) oxalate-phthalate,[5] and thiosulphate with malate and maleate[6] ions were carried out in this laboratory. In continuation of this work the present paper deals with the simultaneous interactions of organic and inorganic ligands with cadmium(II).

2. Theory

Schaap and McMasters[1] applied an extension of DeFord and Hume[7] method for the calculation of consecutive stability constants to the more general system, where more than one kind of ligand was added to the central metal ion to form polynuclear species.

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A complexation reaction of two bidentate ligands X and Y with central metal ion M can be written as :

$$M + iX + jY = MXiYj.$$

The DeFord and Hume expression for $F_0[X]$ may be extended to give a new function F_{00} :

$$F_{00}[XY] = \text{antilog}\ [0 \cdot 4343\ nF\ E_{1/2}/RT + \log\ I_M/I_C]$$

where the symbols have their usual significance.[7]

From Ledens approach[8],

$$\begin{aligned} F_{00}[X, Y] = {} & \{\beta_{00} + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3\}\ [X]^0 \\ & + \{\beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2\}[X] \\ & + \{\beta_{20} + \beta_{21}[Y]\}[X]^2 + \{\beta_{30}[X]^3\} \end{aligned}$$

or,

$$F_{00}[X, Y] = A + BX + CX^2 + DX^3$$

where A, B, C and D are the constants. Polarographic measurements are carried out at such conditions that the concentration of one ligand is kept constant while that of other is varied continuously.

The value of A is obtained from the intercept of the plot of $F_{00}[X, Y]$ vs $[X]$ and new function F_{10} $[X, Y]$ is defined as

$$F_{10}[X, Y] = F_{00}[X, Y] - A/[X] = B + CX + CX^2 + \ldots$$

so that the intercept of $F_{10}[X, Y]$ vs $[X]$ gives the value of B. This process is repeated in a similar manner to get C and D. From these values the stabilities of mixed ligand complex species can be evaluated.

3. Experimental

A Cambridge Automatic Pen Recording Polarograph was used throughout all the experiments. All the chemicals used were of Analar grade. The complexing agents were used in the form of their potassium salts. No maximum suppressor was needed and the polarograms were recorded after deaeration of the test solution of pH 6·6 by purified nitrogen at 25 ± 0·1° C. All half-wave potentials refer to saturated calomel electrode (S.C.E.).

The dropping mercury electrode had the following characteristics :

$t = 3 \cdot 33$ sec. in 0·5 M KCl (open circuit) and

$m = 1 \cdot 75$ mg/sec, $m^{2/3} \times t^{1/6} = 1 \cdot 77$ mg$^{2/3}$ sec.$^{-1/2}$.

4. Results and discussion

Stability constants of single-ligand systems: Literature survey revealed that Cd(II)-malonate[9, 10], Cd(II)-succinate[11] and Cd(II)-thiocyanate[3, 12, 13] systems have been investigated in aqueous medium under varying conditions. These systems were re-investigated in order to obtain data under conditions which are identical to those used in mixed complex studies. The reduction of Cd(II) in the presence of these ligands was found reversible and diffusion controlled. In the studies involving individual ligands, the general procedure[7] was followed. The solutions contained 1 mM Cd(II) and the ligand concentrations were varied as : (MAL] = 0·05 to 0·90 M; [SUCC] = 0·05 to 0·90 M and [SCN] = 0·05 to 1·40 M. The ionic strength was adjusted to 3·0 with potassium nitrate.

The experimental data and F_{i0} [X] values for the single ligand systems have not been included here, only the results obtained are given below :

(1) Cd(II)-malonate complexes :

$\log \beta_1 = 2{\cdot}08$, $\log \beta_2 = 3{\cdot}06 \pm 0{\cdot}04$ and $\log \beta_3 = 3{\cdot}88 \pm 0{\cdot}03$

(2) Cd(II)-succinate complexes :

$\log \beta_1 = 1{\cdot}65$, $\log \beta_2 = 2{\cdot}18 \pm 0{\cdot}06$ and $\log \beta_3 = 3{\cdot}32 \pm 0{\cdot}08$

(3) Cd(II)-thiocyanate complexes :

$\log \beta_1 = 0{\cdot}98$, $\log \beta_2 = 1{\cdot}62 \pm 0{\cdot}03$ and $\log \beta_3 = 1{\cdot}84 \pm 0{\cdot}03$.

These values are in good agreement with the results obtained by other workers,[3,9–13] considering the variations in the experimental set up.

Methylene group decreases the catiophilic property of the carboxylate group because of its buffering action. This effect is present to a greater degree in the succinate ion than in the malonate ion. This particular buffering action of two methylene groups in the succinate ion may probably be the reason for β_1 Cd-SUCC < β_1 Cd-MAL.

Mixed ligand systems

[Cd(II)-malonate-thiocyanate and Cd(II)-succinate-thiocyanate systems]

The two constant concentrations of thiocyanate ions were fixed as : [SCN] = 0·16 and 0·40 M, whereas malonate and succinate concentrations were varied from 0·05 to 0·90 M in each of the systems. Other experimental conditions were identical to those existed in simple systems. Detailed data are given in Tables I and II. In all the above four sets the plots of $- E_{d.e}$ vs log $i/id\text{-}i$ were found to be linear with the slope values lying in the range 30 to 32 mV which shows that the reduction of Cd(II) in the presence of these ligands is reversible and involves two electrons. Direct propertionality between the diffusion current and square root of the effective height of the mercury head proved that the reduction was diffusion controlled.

The shifts in $-E_{1/2}$ values observed in the presence of malonate + thiocyanate and succinate + thiocyanate are greater than those found in presence of malonate or succinate alone (Tables I and II). This conclusively proves the presence of mixed ligand complexes in solution.

Table I

Cd(II) = 1 mM F_{i0} as a function of [MAL] $\mu = 3 \cdot 0$ M (KNO_3)

Concentration of ligand [MAL] M	$-E\frac{1}{2}$ *vs* S.C.E.		$F_{00} \times 10^{-3}$	$F_{10} \times 10^{-3}$	$F_{20} \times 10^{-3}$	$F_{30} \times 10^{-3}$
	0·00 M [SCN]	0·16 M [SCN]				
0·05	0·626	0·639	0·026	0·176	...	...
0·10	0·639	0·648	0·054	0·370	...	...
0·15	0·648	0·653	0·081	0·428	...	...
0·20	0·656	0·657	0·121	0·519	...	...
0·30	0·669	0·676	0·268	0·836	...	...
0·40	0·679	0·691	0·921	2·259	4·872	7·860
0·50	0·686	0·687	1·530	3·026	5·432	7·410
0·60	0·692	0·693	2·307	3·816	5·843	6·860
0·70	0·696	0·698	3·746	5·327	7·167	7·770
0·80	0·701	0·703	5·812	7·244	8·661	8·670
0·90	0·705	0·708	8·531	9·460	8·628	7·670

$\log A = 1 \cdot 23$, $\log B = 2 \cdot 49 \pm 0 \cdot 03$, $\log C = 3 \cdot 24 \pm 0 \cdot 05$ and $\log D = 3 \cdot 88 \pm 0 \cdot 03$

	0·00M [SCN]	M0·40 [SCN]				
0·05	0·626	0·646	0·043	...	...	...
0·10	0·639	0·653	0·078	0·380	...	...
0·15	0·648	0·660	0·142	0·679	...	...
0·20	0·656	0·666	0·233	0·966	...	...
0·30	0·669	0·674	0·523	1·610	...	...
0·40	0·679	0·682	0·942	2·255	...	...
0·50	0·686	0·692	2·222	4·364	7·568	9·736
0·60	0·692	0·698	3·398	5·597	8·361	9·435
0·70	0·696	0·704	5·095	7·221	9·488	9·696
0·80	0·701	0·708	6·908	8·585	10·006	9·132
0·90	0·705	0·714	9·477	10·486	11·006	9·228

$\log A = 1 \cdot 60$, $\log B = 2 \cdot 76 \pm 0 \cdot 02$, $\log C = 3 \cdot 43 \pm 0 \cdot 03$ and $\log D = 3 \cdot 97 \pm 0 \cdot 01$

Table II

Cd (II) = 1 mM F_{i0} as a function of [SUCC] $\mu = 3{\cdot}0$ M (KNO_3)

Concentration of ligand [SUCC] M	$-E\frac{1}{2}$ vs S.C.E. 0·00M [SCN]	0·16M [SCN]	$F_{00}\times10^{-2}$	$F_{10}\times10^{-2}$	$F_{20}\times10^{-3}$	$F_{30}\times10^{-3}$
0·05	0·610	0·630	0·114	1·082	...	...
0·10	0·621	0·639	0·240	1·797	...	...
0·15	0·627	0·644	0·381	2·137	0·358	...
0·20	0·634	0·648	0.522	2·309	0·355	...
0·30	0·645	0·657	1.121	3·537	0·646	1·526
0·40	0·653	0·665	2.181	5·303	0·926	1·839
0·50	0·659	0·672	3·960	7·800	1·240	2·100
0·60	0·666	0·678	6·673	11·021	1·570	2·300
0·70	0·672	0·683	9·974	14·163	1·795	2·292
0·80	0·677	0·689	15·860	19·750	2·269	2·590
0·90	0·682	0·693	19·740	21·867	2·252	2·290

log A = 0·78, log B = 2·20 ± 0·05, log C = 2·28 ± 0·05 and log D = 3·36 ± 0·06

	0·00M [SCN]	0·40M [SCN]				
0·05	0·610	0·641	0·314	2·268	...	...
0·10	0·621	0·648	0·558	3·582	0·782	...
0·15	0·627	0·652	0·808	4·052	0·834	...
0·20	0·634	0·655	1·067	4·335	0·767	2·335
0·30	0·645	0·660	1·539	4·463	0·554	...
0·40	0·653	0·669	3·142	7·355	1·138	2·095
0·50	0·659	0·675	5·567	10·734	1·586	2·572
0·60	0·666	0·681	9·371	15·285	2·080	2·960
0·70	0·672	0·686	14·130	19·900	2·442	3·060
0·80	0·677	0·690	19·370	23·963	2·645	2·930
0·90	0·682	0·694	27·930	30·810	3·112	2·880

log A = 1·30, log B = 2·45 ± 0·05, log C = 2·48 ± 0·02 and log D = 3·42 ± 0·06

The values of A, B, C and D obtained with the help of Schaap and McMasters method[1] for all the systems are given along with the respective tables. From these values, the stability constants were calculated for all the mixed ligand complexes existing in the solution by the usual method.

These are presented below :

	Cd(II)-malonate-thiocyanate	Cd(II)-succinate-thiocyanate
Log β_{11}	3·04 (2·64)	2·91 (2·20)
Log β_{12}	negative	negative
Log β_{21}	3·57 (3·10)	2·50 (2·51)

The values in the parantheses are those which are theoretically predicted stability constants according to the procedure suggested by Watters.[14]

It is seen from these data that the experimentally observed values are higher than the predicted ones except in Cd(II)-succinate-thiocyanate system for β_{21} complex, *i.e.*, $[Cd\,(SUCC)_2\,(SCN)]^{3-}$. Such enhancements may be due to some mutual interactions between the different kinds of ligands in mixed complexes.

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