

POLAROGRAPHIC STUDY OF THE MIXED COMPLEXES OF Cd(II) WITH OXALATE AND MALONATE IONS

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Received April 5th, 1987

The coordinated mixed Cd(II)-oxalate-malonate system has been polarographically studied in aqueous medium. The ionic strength has been maintained constant at $\mu = 1.0 \text{ mol l}^{-1}$ by using NaClO_4 . The overall stability constants, determined by using the Schaap and McMasters method, for the coordinated species $[\text{Cd}(\text{ox})(\text{mal})]^{2-}$, $[\text{Cd}(\text{ox})(\text{mal})_2]^{4-}$ and $[\text{Cd}(\text{ox})_2(\text{mal})]^{4-}$ are respectively $\beta_{11} = 1.3 \cdot 10^4 \text{ l}^2 \text{ mol}^{-2}$, $\beta_{12} = 5.0 \cdot 10^4 \text{ l}^3 \text{ mol}^{-3}$ and $\beta_{21} = 8.7 \cdot 10^4 \text{ l}^3 \cdot \text{mol}^{-3}$. The various coordination equilibria are discussed on the basis of statistical aspects.

In the last years, the study of mixed complexes has received much attention. Their interest has been demonstrated in different fields of research: chemistry, biology, etc¹. The importance of such complexes from the point of view of knowing the peculiarities of metal ion coordination chemistry has been emphasized in numerous reports²⁻¹¹.

In this paper, we attempt to analyse the mixed system Cd(II)-oxalate-malonate at $\mu = 1.0 \text{ mol l}^{-1}$ adjusted with NaClO_4 , as a part of a systematic study of different metallic cations with dicarboxylated ligands^{4,7,9-13}, carried out for the purpose of gaining more insight into them and establishing considerations of a structural nature.

EXPERIMENTAL

Each of the *i*-*E* curves was plotted with a Metrohm E506 polarograph with an E505 polarographic stand. Pt (EA285) and Ag/AgCl/NaCl sat. Metrohm EA427 electrodes were used as counter and reference electrodes, respectively, and the working one was a DME. The temperature in the cell was $25 \pm 0.05^\circ\text{C}$. The ionic strength was adjusted to $\mu = 1.0 \text{ mol l}^{-1}$ with NaClO_4 . Measurements of pH were carried out with a pHM84 digital potentiometer with a GK2401C radiometer combined electrode. With the exception of the solution of Cd(II) in the absence of ligand, which was polarographed at pH 3.5, all the rest were polarographed at pH 7.5 in order to ensure that the concentration of both the oxalate and malonate ions was not below 99% of the total concentrations of their respective salts^{14,15}. The concentration of metal ion was constant at 0.21 mmol l^{-1} in all recordings. Drop-time was controlled at 3.0 s.

The sodium perchlorate, sodium oxalate, and cadmium sulfate were Merck products of p.a. quality, the malonic acid from Carlo Erba R.P.E. and the sodium hydroxide used in the preparation of the sodium malonate and for adjusting the pH was also of p.a. quality from May and Baker.

RESULTS AND DISCUSSION

The plots of $\log [(i_d - i)/i]$ vs E show that the discharges occurred by a reversible two-electron process. The values for the reversible half-wave potentials were directly obtained from these plots.

The Cd(II)-Malonate System

Two experimental studies were carried out. The application of the Deford and Hume method¹⁶ to this coordination system shows that the F_2 vs malonate concentration dependence is a straight line (Fig. 1), which implies the stability of the Cd(mal), $[\text{Cd}(\text{mal})_2]^{2-}$, and $[\text{Cd}(\text{mal})_3]^{4-}$ complexes. The values obtained are given in Table I.

The good agreement allows to propose the following formation constants: $\beta_{01} = 99 \text{ l mol}^{-1}$, $\beta_{02} = 1.5 \cdot 10^3 \text{ l}^2 \text{ mol}^{-2}$, and $\beta_{03} = 4.6 \cdot 10^3 \text{ l}^3 \text{ mol}^{-3}$ in good agreement with those calculated previously for the same system and analogous conditions: $\beta_{01} = 95 \text{ l mol}^{-1}$, $\beta_{02} = 1.3 \cdot 10^3 \text{ l}^2 \text{ mol}^{-2}$, and $\beta_{03} = 6.4 \cdot 10^3 \text{ l}^3 \text{ mol}^{-3}$ (ref.¹⁷).

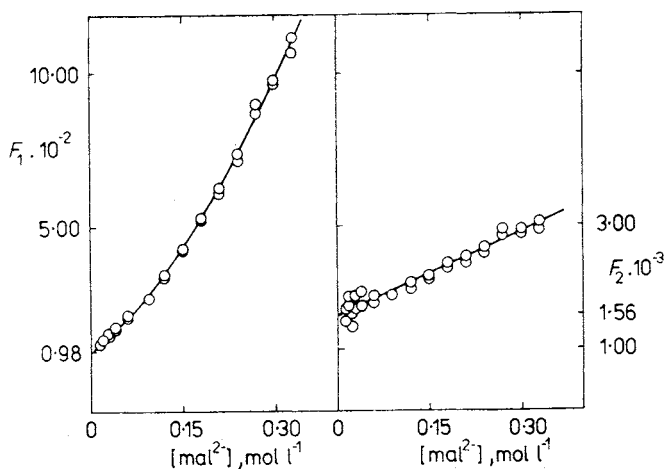


FIG. 1

Plot of the functions F_1 and F_2 vs $[\text{mal}^{2-}]$

The application of the Schaap and McMasters method² to determine mixed complexes requires prior knowledge of the constants of simple complexes, so we have previously¹⁸ studied the simple Cd(II)-oxalate system, the following values being determined: $\beta_{10} = 4.5 \cdot 10^2 \text{ l mol}^{-1}$, $\beta_{20} = 2.1 \cdot 10^4 \text{ l}^2 \text{ mol}^{-2}$, and $\beta_{30} = 1.8 \cdot 10^5 \text{ l}^3 \text{ mol}^{-3}$.

The Mixed Cd(II)-Oxalate-Malonate System

It seems logical from the above to accept that the F_{00} function of Schaap and McMasters presents as maximum the following expression:

$$F_{00} = \{1 + \beta_{01}[\text{mal}] + \beta_{02}[\text{mal}]^2 + \beta_{03}[\text{mal}]^3\} + \\ + \{\beta_{10} + \beta_{11}[\text{mal}] + \beta_{12}[\text{mal}]^2\} [\text{ox}] + \\ + \{\beta_{20} + \beta_{21}[\text{mal}]\} [\text{ox}]^2 + \beta_{30}[\text{ox}]^3. \quad (1)$$

If the concentration of malonate is maintained constant while that of oxalate is varied, the F_{00} function becomes:

$$F_{00} = A + B[\text{ox}] + C[\text{ox}]^2 + D[\text{ox}]^3, \quad (2)$$

where A , B , C , and D are constants. Three experimental studies were carried out. Table II gives the reversible half-wave potentials together with the limiting diffusion currents and the values of the F_{00} , F_{10} , and F_{20} functions at a constant concentration of malonate of 0.02 mol l^{-1} . The plot of the successive F_{10} functions, Fig. 2, confirms the expected linear dependence of the F_{20} function vs $[\text{ox}]$.

The values of A , B , C , and D obtained from the three studies are given in Table III. In each case the value of A calculated from expression (1) agreed satisfactorily with that determined experimentally. The value of D is in acceptable agreement with that obtained from the study of the simple Cd(II)-oxalate system: $\beta_{30} = 1.8 \cdot 10^5 \text{ l}^3 \text{ mol}^{-3}$.

TABLE I
Stability constants of the simple system of Cd(II) with malonate ligand

Exp. No.	β_{01} l mol^{-1}	β_{02} $\text{l}^2 \text{ mol}^{-2}$	β_{03} $\text{l}^3 \text{ mol}^{-3}$
1	98	1 556	4 513
2	100	1 484	4 753

TABLE II

Analysis of the Cd(II)-Na₂ox-Na₂mal-NaClO₄ system in aqueous medium; [mal²⁻] = 0.02 mol l⁻¹. Schaap and McMasters method. Characteristic of the reduction of Cd²⁺ in 1M-NaClO₄: $E_{1/2}^i = 529.3$ mV, $\bar{i}_d = 117.6$ mm

[C ₂ O ₄ ²⁻], mol l ⁻¹	\bar{i}_d , mm	$-E_{1/2}^i$, mV	F_{00}	F_{10}	F_{20}
0.01	115.6	561.6	12.573	897.30	18 730
		561.7	12.671	907.10	19 710
0.015	115.8	567.2	19.409	1 053.9	22 926
		567.0	19.109	1 033.9	21 593
0.03	115.6	579.6 ^a	51.048	1 581.6	29 053
0.04	114.9	584.8 ^a	76.987	1 834.7	28 117
0.05	115.1	590.2 ^a	117.01	2 268.2	31 164
0.06	113.1	594.0	160.07	2 607.8	31 630
		594.6	167.72	2 735.3	33 755
0.07	112.7	598.0	219.32	3 081.7	33 881
		597.2	206.08	2 892.6	31 180
0.08	111.5	601.0	280.00	3 455.0	34 312
		601.6	293.38	3 622.3	36 403
0.09	111	604.8	378.07	4 160.7	38 341
		604.0	355.24	3 907.1	35 523
0.11	111.7	609.8	554.47	5 007.9	39 071
		609.5	541.67	4 891.5	38 013
0.12	110.1	611.8 ^a	657.29	5 447.4	39 478

^a From two measurements.

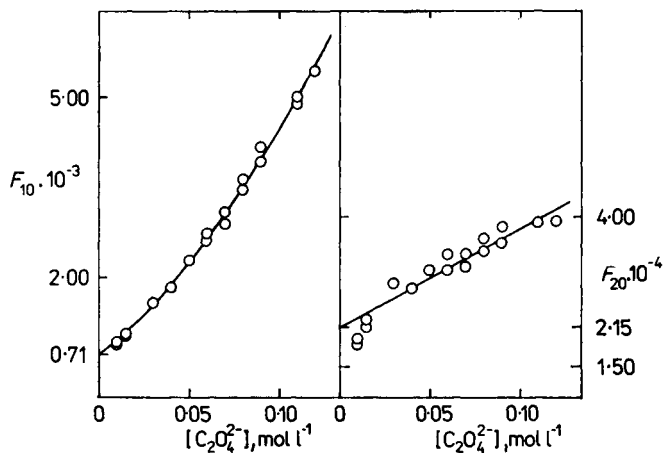


FIG. 2

Plot of the functions F_{10} and F_{20} vs [ox²⁻] [mal²⁻] = 0.02 mol l⁻¹

The data of B , notably greater than $\beta_{10} = 4.5 \cdot 10^2 \text{ l mol}^{-1}$ reveal the presence of mixed complexes with an oxalate ion.

The plot of $(B - \beta_{10})/[\text{mal}]$ vs $[\text{mal}]$, Fig. 3, should give a straight line allowing β_{11} to be obtained from the intercept at $[\text{malonate}] = 0$ and β_{12} from the slope. Calculation by the least squares method gives $\beta_{11} = 1.3 \cdot 10^4 \text{ l}^2 \text{ mol}^{-2}$ and $\beta_{12} = 5.0 \cdot 10^4 \text{ l}^3 \text{ mol}^{-3}$.

Figure 4 shows a linear plot of C vs $[\text{mal}]$ and from the slope we obtain: $\beta_{21} = 8.7 \cdot 10^4 \text{ l}^3 \text{ mol}^{-3}$.

The constants obtained for the mixed complex can be compared with that statistically predictable which was evaluated according to the formulae proposed by Waters¹⁹:

$$\begin{aligned}\beta_{11} &= 2\beta_{20}^{1/2} \cdot \beta_{02}^{1/2} = 1.1 \cdot 10^4 \text{ l}^2 \text{ mol}^{-2} \\ \beta_{12} &= 3\beta_{30}^{1/3} \cdot \beta_{03}^{2/3} = 4.7 \cdot 10^4 \text{ l}^3 \text{ mol}^{-3} \\ \beta_{21} &= 3\beta_{30}^{2/3} \cdot \beta_{03}^{1/3} = 15.9 \cdot 10^4 \text{ l}^3 \text{ mol}^{-3}\end{aligned}$$

in acceptable agreement with the values obtained experimentally. The greatest differences correspond to β_{21} , and seem to point to the low relative stability of the complex $[\text{Cd}(\text{ox})_2(\text{mal})]^{4-}$.

Analysis of the Coordination Equilibria

All the results corresponding to the coordination equilibria of the Cd(II) ion with oxalate and malonate ligands are shown in the Scheme 1. The stepwise constants are logarithmically expressed.

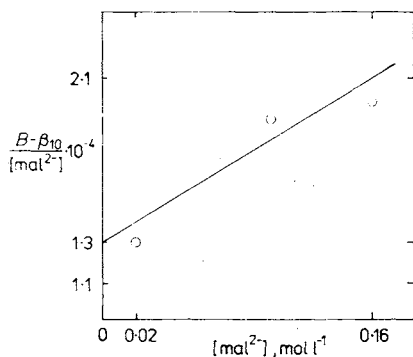


FIG. 3
Calculation of β_{11} and β_{12} for the mixed complexes

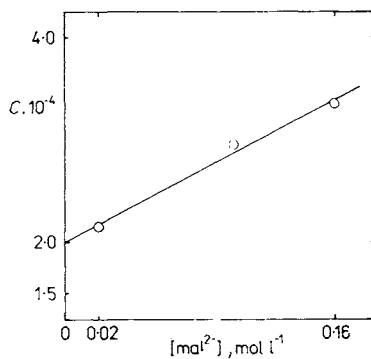
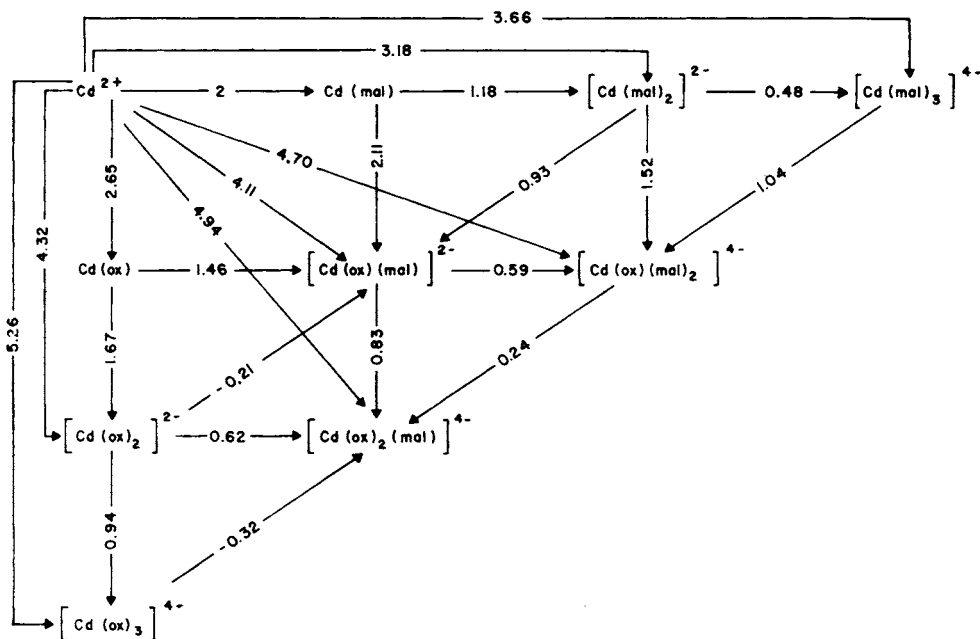


FIG. 4
Plot of coefficient C vs $[\text{mal}^{2-}]$



SCHEME 1

Let us first consider the equilibria of Cd(II) with only one ligand. Table IV gives the values of K_i/K_{i+1} for the Cd(II)-malonate system, Cd(II)-oxalate system and the values expected, taking into account only statistical factors and octahedral coordination²⁰.

The formation of the 1 : 1 complex is greatly favoured by entropic factors while, due to steric effects, the formation of complexes with a greater number of ligands will be progressively hindered, particularly as the length of the chain is increased.

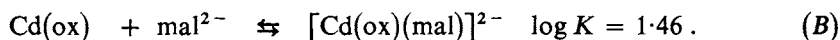
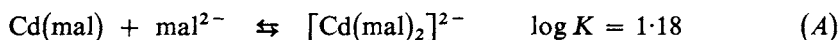
TABLE III

Cd(II)-Na₂ox-Na₂mal-NaClO₄ system. Values of *A*, *B*, *C* and *D*

$[\text{mal}^{2-}]$ mol l^{-1}	<i>A</i>	<i>B</i> · 10 ⁻² l mol^{-1}	<i>C</i> · 10 ⁻⁴ $\text{l}^2 \text{mol}^{-2}$	<i>D</i> · 10 ⁻⁵ $\text{l}^3 \text{mol}^{-3}$
0.02	3.6	7.1	2.15	1.64
0.10	30.7	23.5	2.95	1.62
0.16	74.6	36.2	3.36	2.10

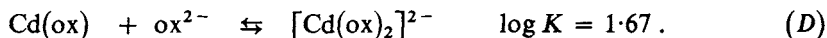
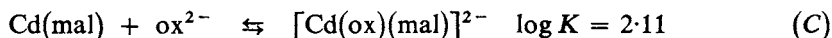
These predictions agree qualitatively with the tendency observed in Table IV for K_1/K_2 , although it is impossible to evaluate their influence quantitatively in order to compare whether the one consideration alone interprets the results obtained. The relative proximity between the values calculated for K_1/K_2 in both cases, and the fact that it diminishes with the ion size increase would be justified by a greater influence of entropic effects. The high values of K_1/K_2 and the relatively low values of K_2/K_3 seem to point to the low relative stability of the complexes with two oxalate or two malonate ligands.

The tendency of the complexes Cd(mal) and Cd(ox) to take a malonate ion as a second ligand is expressed as follows:



Theoretically, taking into account statistical factors alone, it would be expected that the complex $[\text{Cd(ox)(mal)}]^{2-}$ be the more stable, its constant being greater than that of (A) by the statistical factor of 2, ($\log K = 0.301$). The factor found, $\log K = 0.28$, is in good agreement.

The tendency of the same complexes to coordinate an oxalate ion as a second ligand should also be observed:



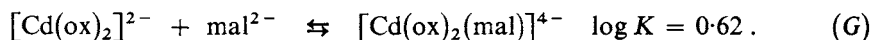
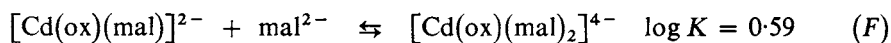
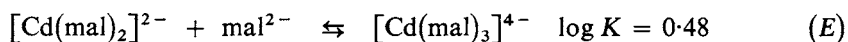
Considerations analogous to those above are valid in this case in which the difference found, $\log K = 0.44$, is also acceptable.

The addition of a third ligand to these complexes is considered as follows.

TABLE IV
Values of K_i/K_{i+1} for the Cd-ligand systems

K_i/K_{i+1}	Statistic	Cd(II)-oxalate	Cd(II)-malonate
K_1/K_2	0.96	9.64	6.45
K_2/K_3	9.75	5.44	5.07

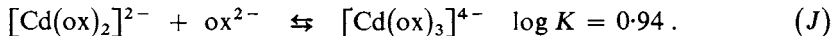
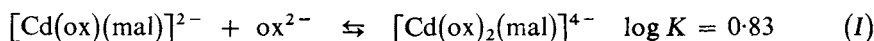
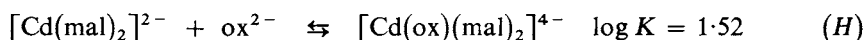
Firstly, the addition of a malonate ion:



Theoretically, the complex $[\text{Cd}(\text{mal})_3]^{4-}$ should be the least stable because it is simple while in the equilibria (F) and (G) mixed complexes are formed. The respective values of K should be in the ratio of the statistical factors $1 : (3/2) : 3$. Between (E) and (F) the statistically expected relation is approximately verified.

The relation between the complex $[\text{Cd}(\text{ox})_2(\text{mal})]^{4-}$ and the complexes $[\text{Cd}(\text{ox})(\text{mal})_2]^{4-}$ and $[\text{Cd}(\text{mal})_3]^{4-}$ is lower than the statistically expected and can be caused by the relatively low stability of the complex $[\text{Cd}(\text{ox})_2(\text{mal})]^{4-}$, as has already been said.

The addition of an oxalate ion to the same complexes is now considered:



The statistically expected ratio of the values of K is $3 : (3/2) : 1$. The values of K for the equilibria (H) and (J) conform to this ratio. The low value of the equilibrium constant (I) suggests the relatively low stability of the coordination species $[\text{Cd}(\text{ox})_2(\text{mal})]^{4-}$.

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