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BEHAVIOUR OF ETHYLENEDIAMINETETRA-ACETATE CHELATES IN THE PRESENCE OF OTHER METALLIC CATIONS

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Upon certain potentiometric and polarographic evidence it has been postulated that the stability of EDTA chelates is greatly reduced by the interaction, or even complexing, of a second metallic cation. A study is made of EDTA solutions containing several pairs of divalent cations and it is shown that the results of this investigation provide no evidence to support the above view since it is possible to account for the behaviour of such systems by a consideration of the known formation constants and solubility products of the ionic species present.

The formation constants of the chelates of many metal cations with ethylenediaminetetracetic acid (EDTA) have been determined 1, 2 by methods based on the ability of one ion to displace another from its chelate of known formation constant. Pfeiffer and Schmidt,³ however, showed that in systems containing EDTA and two metal cations it is possible, under certain conditions, to precipitate that ion which forms the strongest chelate, and investigating the copper chelate in the presence of other cations, these authors state that from polarographic evidence it must be concluded that there is an interaction between the complex anion and added cation sufficiently great to weaken the complex bonding of the copper ion. It has since been suggested ⁴ that this phenomenon might be interpreted as indicating either a very strong ion-dipole interaction, or that both metal cations are chelated by the EDTA molecule in the manner suggested by Schwarzenbach and Ackermann ⁵ for homologues of EDTA.

Polarographic investigations of the kinetics of ion exchange in EDTA chelates ^{6,7} have not provided any information concerning the formation of the postulated double chelates or ion-ion associations, though it is clear that their formation should be readily detected when both metal cations are reducible at the dropping mercury cathode.

In the present work, a detailed study was made of the polarographic behaviour of a number of EDTA solutions containing different pairs of metallic cations, and the results were compared with those obtained from potentiometric, spectrophotometric and conductometric examinations of the same systems.

EXPERIMENTAL

Polarograms were usually recorded on an undamped Radiometer Polarograph (type PO34) but those shown in fig. 1 were recorded manually, the applied potentials being measured using a Cambridge pH meter as a valve potentiometer. Redistilled washed mercury was used for the dropping cathode and solutions were gassed with nitrogen for 10 min before electrolysis. Diffusion currents were determined from reduction wave heights which had been corrected for the residual current in accordance with the usual procedure,⁸ and the accuracy of the determinations was between 0.5 % and 1 %. The reproducibility of experiments was found to lie within the observed experimental error. Experiments were carried out at a temperature of $25 \pm 0.7^{\circ}$ C.

pH measurements were made with a Cambridge pH meter, using the Cambridge Alki glass electrode for pH values greater than 9. Spectrophotometric data were obtained using a Hilger Uvispec, and conductometric data using a Mullard conductivity bridge, type E7566.

All substances used were of A.R. grade. The disodium salt of EDTA was kindly presented by Messrs. Versenes Inc.

RESULTS AND DISCUSSION

POLAROGRAPHIC DATA

In fig. 1 are shown three polarograms obtained in the titration of $CdSO_4$ into a solution containing 2 mM CuSO₄ and 1 mM EDTA in 0.2 M acetate buffer pH 4.71. The three reduction waves observed were easily identified as being due to the discharge of free Cu²⁺ ions, chelated copper ions, and free Cd²⁺ ions. The cadmium—EDTA chelate is not reduced at the dropping mercury cathode.

From curves (ii) and (iii) it is seen that no Cd^{2+} reduction wave appeared until the added $CdSO_4$ was in approximately 1 mM concentration, i.e. equal to that of the copper—EDTA chelate. The wave due to the copper chelate tended to become drawn out in shape in the presence of Cd^{2+} ions, with a small change in half-wave potential.

The experiment was repeated using $ZnSO_4$ in place of $CdSO_4$ and similar polarograms were obtained. The variation of the diffusion current due to free Zn^{2+} ions with total added concentration of $ZnSO_4$ is shown in fig. 2, where the i_d against C curve for Zn^{2+} ions alone is also drawn. The asymptote to the experimental curve has the same slope as the i_d against C line, and extrapolation back to zero diffusion current gives a total zinc concentration approximately equal to that of the EDTA present.

An examination of the dependence of the diffusion currents due to both free Zn^{2+} and Cd^{2+} ions upon height of the mercury reservoir showed that they were diffusion and not kinetically controlled.⁹

One possible interpretation of the above results is that they represent formation of a double chelate

 $CuY^{2-} + Cd^{2+} \rightleftharpoons CuYCd$



FIG. 1.—Polarograms of 2 mM CuSO₄, 1 mM EDTA in 0.2 M, acetate buffer pH 4.71. Curve (i) no Cd²⁺ added, (ii) added Cd²⁺, 1 mM, (iii) added Cd²⁺, 2 mM.



FIG. 2.—Relation between diffusion current due to free Zn^{2+} ions and total concentration of added ZnSO₄. Curve (i): i_d against C curve for Zn^{2+} ions alone; curve (ii): Zn^{2+} ions in presence of 2 mM CuSO₄ and 1 mM EDTA; $m^{\frac{3}{2}t} = 2.36$ mg^{$\frac{3}{2}$} sec^{$\frac{1}{2}$}.

(where Y^{4-} is the tetravalent EDTA anion) from which copper is irreversibly reduced at the dropping cathode. Cd^{2+} ions (or Zn^{2+} ions) in excess of those associated with the copper—EDTA chelate are discharged normally.

By adding a large excess of $CdSO_4$ to a solution of the copper chelate containing initially no excess free Cu^{2+} ions, it was shown that Cu^{2+} ions were released from the chelate. The variation of concentration of free Cu^{2+} ions with total concentration of added Cd^{2+} ions, expressed in table 1, provides a method for the determination of the formation constant of the suggested complex CuYCd.

TABLE 1.—1 mM Cu—EDTA CHELATE IN 0.2 M ACETATE pH 4.71

added CdSO4 (mM)	free Cu ²⁺ ions (mM)	
0	0	
4	0.12	
8	0.22	
20	0.33	
40	0.46	

Considering the equilibria,

$$Cu2+ + Y4- \rightleftharpoons CuY2-,$$

$$Cd2+ + Y4- \rightleftharpoons CdY2-,$$

$$Cd2+ + CuY2- \rightleftharpoons CuYCd.$$

we then have that

$$Y = \Sigma [H_nY] + [CuY^{2-}] + [CdY^{2-}] + [CuYCd]$$

$$C = [Cd^{2+}] + [CdY^{2-}] + [CuY] + [Cd]$$

$$S = [Cu^{2+}] + [CuY^{2-}] + [CuY] + [Cd]$$

where Y, C and S are respectively the total concentrations of EDTA, cadmium and copper present in the system, and $\Sigma[H_nY]$ is the sum of the concentrations of the unchelated ionic species of EDTA.

When the added cadmium is in great excess we can ignore the term $\Sigma[H_nY]$, and put as an approximation $[Cd^{2+}] = C$.

Solving the above equations we then obtain, when Y = S,

$$rac{K_1}{K_2}\left(1/C+K_3
ight)=rac{Y-[\mathrm{Cu}^{2+}]}{[\mathrm{Cu}^{2+}]^2}$$
 ,

where K_1 , K_2 , K_3 are the formation constants of CuY²⁻, CdY²⁻ and CuYCd respectively.

A plot of $\frac{Y - [Cu^{2+}]}{[Cu^{2+}]^2}$ against 1/C should give a straight line of slope K_1/K_2

and intercept K_3K_1/K_2 . Since the experiments to determine $[Cu^{2+}]$ for different values of C were carried out in acetate medium in which complexes with both Cu^{2+} and Cd^{2+} ions are formed, this introduces the difficulty that the values of K_1 and K_2 are not known. However, the actual values are not required for the determination of K_3 , it being sufficient that they are constant.

The experimentally determined curve is shown in fig. 3, and it is compared with the curves which would have been obtained for the same value of K_1/K_2 but different values of K_3 .

It is seen that K_3 has a value ~ 0 , and that K_1/K_2 has the reasonable value of 119. (The formation constants of the copper and cadmium chelates in non-complexing aqueous solution are given as $10^{18\cdot4}$ and $10^{16\cdot5}$ respectively.) It must be concluded that the formation of a double chelate cannot account for the polarographic effects observed here.

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There is, however, an alternative and somewhat more reasonable interpretation of these effects. Kolthoff and Lingane 10 give a number of instances in which the reduction product of one electrode reaction may react with another reducible substance present in such a manner that prevents the reduction of the second substance more or less completely.

In the copper—EDTA—cadmium system it must be noted that free Cd^{2+} ions are reduced at a potential more negative than the chelated copper so that free EDTA anions are present in the vicinity of the mercury cathode surface at the potential at which Cd^{2+} ions are reduced. In this case the electrode reactions may be represented by

$$CuY^{2-} + 2e \rightleftharpoons Cu(Hg) + Y^{4-},$$

 $Cd^{2+} + Y^{4-} \rightleftharpoons CdY^{2-}$,



FIG. 3.—Relation between $1/C \text{ (mM}^{-1)}$ and $\frac{Y - [Cu^{2+}]}{[Cu^{2+}]^2} \text{ (mM}^{-1)}$ compared with lines for $K_3 = 10$ and 100.

the net electrode process tending to be irreversible on account of the high stability constant of CdY^{2-} (pK 16.5). There should be no Cd^{2+} ions in a reducible form at the electrode surface until the total concentration of cadmium present exceeds that of EDTA.

A certain measure of support for this view is that when Cd^{2+} ions are titrated into a solution of the nickel—EDTA chelate (which has the same formation constant as the copper chelate, pK 18·4), the measured diffusion current due to free Cd^{2+} ions follows the i_d against C curve for Cd^{2+} ions alone. Since Ni²⁺ ions are reduced at a potential more negative than the free Cd^{2+} ions, there can be no interfering electrode reaction in this case. Pfeiffer and Schmidt ³ give no details of their polarographic evidence for the lowering of the stability of the Cu—EDTA chelate in the presence of zinc ions and it appears that they based this conclusion on the change in the half-wave potential of the Cu—EDTA wave when zinc ions were added.

POTENTIOMETRIC DATA

Although the copper—EDTA chelate is completely stable in strong NaOH or KOH, it has been shown ³ that when Zn^{2+} , Ca^{2+} , Sr^{2+} , Be^{2+} or Mg^{2+} ions are added, copper hydroxide precipitates at pH values between 6 and 11. In view of the very low solubility product of Cu(OH)₂ and the fact that these other divalent cations themselves form chelates with EDTA, it might be possible to account for the observed precipitation of copper hydroxide by a consideration of the simple displacement of copper from its chelate by the added cation.

Considering the equilibrium

$$\begin{array}{l} Cu^{2+}+Y^{4-}\rightleftharpoons CuY^{2-}\text{,}\\ M^{2+}+Y^{4-}\rightleftharpoons MY^{2-}\text{,} (M^{2+}\text{ is the added metallic cation),} \end{array}$$

in a system where the total concentration of EDTA, Y, is equal to that of copper C, if the formation constant of MY^{2–}, K_4 , is much less than that of the copper chelate K_1 , we may put

$$Y \approx [CuY^{2-}] = K_1[Cu^{2+}][Y^{4-}],$$

[Cu²⁺] = [MY²⁻] = K₄[M²⁺][Y⁴⁻].

and

$$[Cu^{2+}] = C/\alpha^{\frac{1}{2}}$$
, where $\alpha = K_1/K_4$

and hence precipitation of Cu(OH)₂ will occur when

$$[OH^{-}] \ge (S/C)^{\frac{1}{2}} \alpha^{\frac{1}{2}}$$

where S is the solubility product of copper hydroxide, [Cu][OH-]². Seidell ¹¹ quotes the value of $S = 3 \times 10^{-19}$, and $\alpha = K_1/K_4$ may be determined from the values listed by Martell and Calvin.¹²

Potentiometric titration of KOH into a solution of $CuSO_4$, EDTA and the added metal, each in 50 mM concentration showed that $Cu(OH)_2$ precipitated at the pH values given (to the nearest 0.5 pH unit) in table 2. In the last column are shown the pH values calculated from the above expression.

TABLE 2

metal	log ₁₀ formation constant of chelate (K ₄)	pH of Cu(OH) ₂ precipitation	
		observed	calculated
Cd ²⁺	16.5	6.0	6.0
Zn ²⁺	16.2	6.5	6.0
Ca ²⁺	10.6	9.0	7.5
Mg ²⁺	8.7	10.0	8.0
Na+	1.66	no precipitation	9.5

It is seen that the discrepancy between theoretical and observed pH values becomes large above pH 9. However, in strongly alkaline solutions one must consider the further equilibria,

$$Cu2+ + 2OH- \rightleftharpoons CuHO2- + H+,CuHO2- \rightleftharpoons CuO22- + H+,CuY2- + OH- \rightleftharpoons Cu(OH)Y3-.$$

Data on the first two are given by McDowell and Johnston ¹³ and on the third by Bennett and Schmidt.¹⁴ From this, it may be shown that the equilibrium constants have the values,

$$K_{5} = \frac{[H^{+}][CuHO_{2}^{-}]}{[Cu^{2+}][OH^{-}]^{2}} \approx 1,$$

$$K_{6} = \frac{[CuO_{2}^{2-}][H^{+}]}{[CuHO_{2}^{-}]} = 8 \times 10^{-14},$$

$$K_{7} = \frac{[CuOHY^{3-}]}{[CuY^{2-}][OH^{-}]} = 2 \times 10^{2}.$$

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It may be readily shown that in the first equilibrium above, the formation of $CuHO_2^-$ becomes significant at pH 9, and with the above values for K_5 , K_6 and K_7 , the calculated pH values for the precipitation of $Cu(OH)_2$ approximate to those observed. It may also be shown that copper hydroxide will not precipitate from a solution of the EDTA chelate alone even at pH 14. The agreement with experimental results to 0.5 pH unit is as good as can be expected in view of the approximations made.

FURTHER DATA AND CONCLUSIONS

The double chelate structure proposed by Martell and Calvin ⁴ for the coppercalcium–EDTA system involves separate action of the two tridentate aminodiacetate groups of the chelating agent, both metallic cations being complex bonded, and it was suggested that tridentate bound copper might well be more readily dissociated than the tetradentate chelate formed in the presence of alkali metals.

It might be expected then that the formation of such a double chelate from the normal CuY^{2-} chelate upon addition of Ca^{2+} ions should be accompanied by a change in the intensity of u.-v. absorption, reflecting the change in copper bonding, and by a change in the molar conductance, reflecting the formation of an uncharged species from the simple cation and complex anion. Pfeiffer and Schmidt³ found no difference between the u.-v. absorption spectra of the disodium and calcium salts of the copper—EDTA chelate and concluded that the copper was bonded in much the same way in both compounds.

In our present investigation it was found that the presence of many other added metals did not appreciably change the u.-v. absorption spectrum of the copper chelate, and it was found that the measured increases in molar conductance of solutions of the copper chelate in various concentrations, when other metallic cations were added, followed those expected on the assumption that the metals remained in solution as free ions.

Schwarzenbach and Ackermann,⁵ studying homologues of EDTA, have shown that when the two donor N atoms are separated by four > CH_2 groups, as in tetramethylenediaminetetra-acetic acid, it is possible for the molecule to chelate weakly a second metallic cation, but that this phenomenon could not be detected with EDTA. In accordance with this work, results of the present investigation have provided no evidence to support a view that the EDTA molecule may complex more than one metal, and have, in fact, suggested that the observed behaviour of EDTA chelates in presence of other metallic cations may be accounted for by a consideration of the formation constants and solubility products of the various ionic species present.

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