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INVESTIGATION OF COPPER(II) CHELATES OF EDTA AND DTPA
WITH CUPRIC-SELECTIVE ELECTRODES

by

SRL
RECORDS SECTION

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INVESTIGATION OF COPPER(II) CHELATES OF EDTA AND DTPA
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ABSTRACT

Recently developed cupric-selective electrodes, which enable direct determination of uncomplexed cupric ion in solution, were used to investigate the Cu-EDTA and Cu-DTPA systems in 0.1M KClO₄ at 25°C. Stability constants for formation of CuY, CuH_nY, and Cu₂Y (where Y is either EDTA or DTPA) were calculated from pH and pCu measurements. Log K was 19.19 ±0.04 for Cu-EDTA and 21.45 ±0.10 for Cu-DTPA. The behavior of cupric-selective electrodes in these systems is discussed.

* The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

INTRODUCTION

Accurate determination of stability constants of metal chelates such as those of copper(II) with ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) is difficult because of the high stability of the metal complexes and because of the variety of acid and metal species that must be taken into account. Past methods of investigation have been indirect [1-4]: the classic chelon displacement method of Schwarzenbach uses pH measurements, and the mercury electrode method uses the mercury chelate as the basis of comparison. Recently developed cupric-selective electrodes offer a new approach to studying these systems through direct determination of the uncomplexed cupric ion in solution. This paper describes investigation of the Cu-EDTA and Cu-DTPA systems with cupric-selective electrodes.

EXPERIMENTAL

REAGENTS

All solutions were made with deionized water and stored in polyethylene bottles. NaOH solution was prepared CO₂-free by the method of Kolthoff [5]. 0.1M NaOH and 0.1M HClO₄ were standardized by conventional methods. 0.1M Cu(ClO₄)₂ was standardized against Na₂H₂EDTA by neutralization of the acid released and by potentiometric titration with the cupric-selective electrode as the indicator.

The EDTA was "Ultrex"* grade. The DTPA (Baker) was recrystallized twice from hot water. Both solids were dried at 105 to 110°C for 2 hours and stored in a desiccator. The purity of the chelon acids was confirmed by alkalimetric titration of determinate solutions in the presence and the absence of equimolar $\text{Cu}(\text{ClO}_4)_2$.

Acid constants were determined for solutions of 0.001M chelon acid in 0.1M KNO_3 . Solutions for the titration experiments in determination of copper constants contained 0.1M chelon acid, with sufficient NaOH added to obtain dissolution.

The solid salt CuH_3DTPA was prepared from equimolar quantities of chelon acid and CuCl_2 or CuSO_4 , mixed in sufficient water to dissolve the product. The CuH_3DTPA was precipitated from the aqueous solution by addition of ethanol; the product was recrystallized twice and then dried for 4 hours at 110°C. The composition was confirmed by determining the carbon, hydrogen, and nitrogen contents by combustion; by titrating the acid hydrogens with NaOH; and by determining the copper content by atomic absorption spectrometry and by EDTA titration after radiolytic destruction of DTPA with ^{60}Co , as described by Bibler [6].

APPARATUS

Two Orion** cupric-selective electrodes with solid membranes of $\text{CuS-Ag}_2\text{S}$ were used for most of this work. Orion-1 was an older

* Registered tradename of J. T. Baker Chemical Company.

** Orion Research Incorporated.

(1968) Model 94-29-00 with a large diameter barrel; Orion-2 was the newer (1972) Model 94-29A. The Radiometer "Selectrode"* Model F 1112 Cu, which has a CuSe membrane, was used during the later stages of the Cu-DTPA investigation. The glass electrode was Beckman** Research Model 39004, and the reference electrode was Orion Double Junction Model 90-02-00 with 10% KNO₃ in the outer compartment. Potentials were measured by an Orion Model 801 digital pH meter.

The test solution was contained in a 100-ml polypropylene beaker with a polyethylene lid drilled to accommodate the electrodes, the tip of a microburet, and tubing for N₂. The solution was stirred with a "Teflon"†-coated magnetic stirring bar and was maintained at 25°C in a water bath.

PROCEDURE

Solutions of 0.1M ionic strength were used throughout the experiments. Although the electrodes respond to activities, measurements were interpreted in terms of molar concentrations, which are assumed proportional to activities at constant ionic strength.

The glass and copper electrodes were calibrated daily in the appropriate supporting electrolyte that contained known concentrations of HClO₄ and/or Cu(ClO₄)₂. The response of the copper electrodes in 0.1M KClO₄ or 0.1M KNO₃ was the theoretical 29.6 mV

* Registered tradename of Radiometer A/S, Copenhagen.

** Beckman Instruments, Inc.

† Registered tradename of E. I. du Pont de Nemours and Co.

per decade of concentration; the effect of pH was not significant. The concentrations (c) of H^+ and Cu^{2+} in the experimental solutions were calculated from the measured potentials, E, by the Nernst relationship

$$E = \epsilon + \frac{RT}{zF} \ln c$$

after the constant ϵ was established by calibration. The value of ϵ for each electrode varied only 1 to 2 mV throughout the work, and no trends were observed.

Measurements in the test solutions were made with the two Orion electrodes, the Radiometer "Selectrode," and the glass electrode, connected to the common reference electrode through a switch box.

Acid stability constants were measured in a solution containing a known quantity of NaOH or $HClO_4$ added to 50 ml of the 0.001M chelon acid in 0.1M KNO_3 . The hydrogen ion concentration was determined with the calibrated glass electrode.

Cupric stability constants were determined in the test solutions containing 50 ml of 0.1M $KClO_4$ with $\sim 10^{-3}M$ EDTA or DTPA and >99% of the equivalent amount of $Cu(ClO_4)_2$; the pH was adjusted to the desired value. Most titrations, except a few at low pH, were conducted after the copper electrodes were preconditioned by soaking overnight in the test solution. Appropriate microliter increments of $Cu(ClO_4)_2$ were then added, the pH was adjusted as needed with NaOH or $HClO_4$ from a microburet, and the potentials of the Cu electrodes were determined. The electrodes responded

satisfactorily to these additions, but near the equivalence point as much as 10 minutes were required to obtain a reading that did not drift. The equivalence point was the calculated inflection point of the titration curve.

Other measurements were made in 10^{-2} to 10^{-4} M solutions of the CuH_3DTPA in 0.1M KClO_4 , with appropriate pH adjustment or $\text{Cu}(\text{ClO}_4)_2$ additions.

CALCULATIONS

All species are given in molar concentrations, and all stability constants are given in terms of concentrations, not activities. For simplicity, charges have been omitted. Y refers to either EDTA or DTPA.

Stability constants for the chelon acids were obtained from neutralization curves by the method of Bjerrum [7], which assumes successive addition of protons to the chelon anion. The average number of replaceable hydrogens per ligand, \bar{n} , which is related to the overall stability constants, β_i , can be calculated from experiment by

$$\bar{n} = \frac{nY_T - H - c_B + c_A + k_w/H}{Y_T} \quad (1a)$$

$$= \frac{\sum_{i=1}^n i\beta_i H^i}{\left(1 + \sum_{i=1}^n \beta_i H^i\right)} \quad (1b)$$

where n is the number of acid hydrogens of the chelon

H is the measured hydrogen ion concentration

c_B and c_A are the concentrations of added NaOH and HClO₄, respectively

k_w is the ion concentration product of water; (the value determined by Harned [8] for 0.11M KCl was used)

Y_T is the total concentration of chelon

β_i is the overall acid stability constant, defined by

$$\beta_i = \frac{(H_i Y)}{(Y)(H)^i} \quad (2a)$$

$$= \prod_{j=1}^i k_j \quad (2b)$$

where K_j are the constants for successive addition of protons to the ligand Y:

$$k_j = \frac{(H_j Y)}{(H_{j-1} Y)(H)} \quad (3)$$

Experimental values of \bar{n} as a function of pH (Figure 1) were numerically fitted to obtain β_n by a method used previously [9].

The following general relationships were used in calculation of stability constants for the CuY systems. The species Cu₂Y, CuH₃Y, and H₅Y were not considered in the interpretation of the

EDTA system.

$$Cu_T = Cu + 2 Cu_2Y + \sum_{n=0}^3 CuH_n Y \quad (4)$$

$$Y_T = Y^* + Cu_2Y + \sum_{n=0}^3 CuH_n Y \quad (5)$$

$$Y^* = \sum_{i=0}^5 H_i Y \quad (6a)$$

$$= Y \left(1 + \sum_{i=1}^5 \beta_i H^i \right) \quad (6b)$$

$$= Y \alpha \quad (6c)$$

$$A = \frac{(Cu_2Y)}{(Cu) (CuY)} \quad (7)$$

$$B_n = \frac{(CuH_n Y)}{(CuH_{n-1} Y) (H)} \quad (8)$$

$$K_n = \frac{(CuH_n Y)}{(Cu) (H_n Y)} \quad (9)$$

where Y_T and Cu_T are the total amounts of chelon and copper respectively, and A , B_n , and K_n define the constants to be determined.

The formation constant, A, for Cu_2Y was determined at pH 7 to 8, with $2Y_T > \text{Cu}_T > Y_T$, where it is assumed that protonated copper species and Y^* can be neglected. Then

$$\text{Cu}_T = \text{Cu} + \text{CuY} + 2 \text{Cu}_2\text{Y} \quad (10)$$

$$Y_T = \text{CuY} + \text{Cu}_2\text{Y} \quad (11)$$

The calculated CuY and Cu_2Y are combined with the measured Cu to determine A directly.

The B_n values were determined by the Bjerrum treatment of the system in which CuY is the species that adds protons [4]; then \bar{n} , the average number of bound protons, is

$$\bar{n} = \frac{(H_T - H)}{\sum_{n=0}^{n=3} \text{CuH}_n\text{Y}} \quad (12)$$

The relationship of \bar{n} to the B_n 's and H is analogous to Equation (1b) and (2b). The values of B_n were obtained by fitting the formation curves in Figure 2.

The determined values of A and B_n were used with Cu and H concentrations, measured at the equivalence point in the titrations, to determine CuY :

$$\text{CuY} = \frac{(\text{Cu}_T - \text{Cu})}{1 + 2A\text{Cu} + B_1H + B_1B_2H^2 + B_1B_2B_3H^3} \quad (13)$$

At the equivalence point, $Y_T = Cu_T$; then

$$Y^* = Cu [1 + A(CuY)] \quad (14)$$

$$K_o = \frac{(CuY) (\alpha)}{(Cu)^2 [1 + A (CuY)]} \quad (15)$$

The remaining K_n values are related to the other constants by:

$$K_n = \frac{K_o \prod_{i=1}^n B_i}{\beta_n} \quad (16)$$

RESULTS AND DISCUSSION

BEHAVIOR OF CUPRIC-SELECTIVE ELECTRODES

Although the cupric-selective electrodes have been used as indicators in potentiometric titrations of Cu and EDTA [10], they were not suitable for direct quantitative determination of uncomplexed copper in the present chelon systems. In the presence of excess EDTA or DTPA, the electrodes were slow to stabilize. Reliable measurements under such simplifying experimental conditions as a chelon-to-copper ratio of 2:1 were not possible because the potential continued to drift downward at a rate of a few tenths of a mV per hour, even after 24 hours of equilibration. However, when there was only a small excess of chelon over copper (~1%),

the potential would stabilize sufficiently overnight to enable a potentiometric titration to be made, with the cupric electrode as indicator. With excess copper over chelon, the electrode response was rapid and stable.

Even in the presence of stoichiometric amounts of Cu and Y, the response of the electrodes in direct measurements (without the preconditioning described above) was questionable. For example, in solutions of the salt CuH_3DTPA , the electrodes indicated lower uncomplexed copper concentrations as more CuH_3DTPA was added at constant pH. This behavior was still evident at pH 2 where the expected copper concentration was above the limit of sensitivity of the electrodes.

There were indications that the sensitivity limit of the electrodes was approached or exceeded, particularly in the DTPA system at higher pH values. The uncomplexed copper concentration decreases as the pH increases. This limitation is illustrated in Figure 3 where the observed pCu as a function of pH is compared. For the DTPA system, the observed pCu falls off above pH 4; this caused the low K_o values reported in the next section.

The Orion CuS electrodes were more sensitive than the Radiometer CuSe "Selectrode," which gave higher copper concentrations in the few titration experiments in which it was used (Table I). In the presence of excess copper (i.e., in the experiments to determine A, shown in Table II), the copper concentrations determined by the Radiometer "Selectrode" were high, but agreed with the Orion electrodes within the expected experimental error.

STABILITY CONSTANTS

The acid stability constants for the chelons in 0.1M KNO_3 at 25°C agreed with literature values (Table III). These values were used in the calculations for the copper systems.

Perchlorate, rather than nitrate, was chosen as the anion for the copper investigations to minimize possible perturbations from copper-anion interactions. Table IV summarizes all stability constants of copper with EDTA and DTPA derived from this work and compares them with published values. The K_n values for EDTA are higher than those previously obtained [1], and K_n values for DTPA are higher than some numbers reported [3,4]. Many of the constants listed are interrelated; those determined independently are K_0 , A, and the B_n 's.

Table I gives typical experimental data used to calculate K_0 . The scatter of results and their variation with pH of the test solution is shown in Figure 4. In the EDTA system there was no trend with pH, and the reported K_0 is the average for pH 1 to 5, the entire range investigated. For DTPA there was a definite drop in the calculated K_0 above pH 4.2, because, as discussed earlier, the copper concentration to be measured fell below the sensitivity of the electrode. Therefore, for DTPA, the K_0 values between pH 2 and 4.2 were averaged. The wide scatter of all data was principally due to the precision of the measured copper, which is squared in the calculation (Equation 15).

Formation of the bimetallic complex with DTPA, but not with EDTA is indicated by the calculated and observed titration curves (Figure 5). These typify those for the titration experiments, except that at higher pH it was necessary to reduce the concentration of the titrant ten or a hundredfold to obtain sufficiently small incremental changes of potential for accurate computation of the inflection point. The calculated curves assume that only 1-1 complexes are formed. For EDTA, calculated and observed behavior agreed very well, which confirms the presence of only 1-1 complexes and also attests to the accuracy of the response of the cupric electrode. For DTPA, no similar abrupt change in potential occurred, and the calculated curve does not agree with the experimental one. This lack of agreement and, in particular, the failure to respond to the excess copper added, indicated the presence of Cu_2DTPA .

In Table II are given experimental data from which A, the formation constant for Cu_2DTPA , was derived. The final value of A was the average of the values obtained by the two Orion electrodes and the Radiometer "Selectrode."

The final values reported for the formation constants of CuY , and hence of the other species, depend not only on experimental data taken in the metal systems, but also on data from the acid chelon systems, because the acid dissociation constants are included in the calculations. These acid values in turn depend

on the value chosen for the ion product of water, k_w , and on the supporting electrolyte. If there is complexation with the supporting electrolyte, the first acid constant will be affected [11]. To obtain a direct comparison of the experimental systems of this and other work for the copper chelate systems only, the contribution of the acid stability constants was eliminated from K_0 by dividing by the α values derived from the respective acid formation constants (Equation 15). In Table V, the results at pH 3, 5, and 7 demonstrate that the discrepancies come from measurements in the copper systems and not from the acid constants used for the computations.

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TABLE I

Typical Experimental Data for K_0 Determination

pH	pCu _T	Orion-1		Orion-2		Radiometer "Selectrode"	
		pCu	log K_0	pCu	log K_0	pCu	log K_0
<i>Cu-EDTA</i>							
1.303	2.819	4.169	19.007	4.233	19.137		
2.023	3.043	5.034	19.108	5.024	19.088		
2.537	3.015	5.548	19.201	5.578	19.261		
2.975	3.009	6.055	19.434	6.028	19.380		
3.457	3.006	6.427	19.309	6.444	19.343		
3.977	3.008	6.917	19.303	6.893	19.256		
4.481	3.016	7.289	19.058	7.316	19.112		
4.931	3.042	7.739	19.054	7.793	19.162		
<i>Cu-DTPA</i>							
1.331	2.988	4.270	21.894	4.236	21.825		
2.086	2.986	5.286	21.857	5.331	21.947		
2.735	2.437	6.336	21.560	6.244	21.376	6.183	21.254
3.318	2.442	7.441	21.810	7.482	21.892	7.052	21.031
3.724	3.183	7.543	20.781	7.741	21.178		
4.172	2.964	8.486	21.431	8.533	21.525		
4.589	2.694	8.653	20.727	8.784	20.990		
5.485	2.973	9.480	20.430	9.636	20.742		

TABLE II

Determination of Formation Constant of Cu_2DTPA

pH	pCu _T	pY _T	Orion-1		Orion-2		Radiometer "Selectrode"	
			pCu	log A	pCu	log A	pCu	log A
6.981	3.226	3.395	6.831	6.705	6.784	6.786	6.750	6.705
7.305	3.520	3.689	6.905	6.859	6.845	6.799	6.797	6.751
7.345	3.220	3.395	6.902	6.894	6.844	6.836	6.794	6.786
7.521	3.226	3.395	6.845	6.799	6.801	6.756	6.780	6.736
7.787	3.226	3.395	6.858	6.819	6.743	6.685	6.804	6.759
7.803	3.520	3.689	6.936	6.892	6.868	6.823	6.833	6.789
Average log A				6.84		6.78		6.76
σ				0.03		0.04		0.02

Overall average of log A = 6.79

TABLE III

Acid Stability Constants of EDTA and DTPA

<u>log k₁</u>	<u>log k₂</u>	<u>log k₃</u>	<u>log k₄</u>	<u>log k₅</u>	<u>Conditions</u>	<u>Reference</u>
<i>EDTA</i>						
10.27	6.19	2.79	1.99	-	0.1M KNO ₃ (25°C)	This work
10.26	6.16	2.67	2.00		0.1M KCl (20°C)	12
<i>DTPA</i>						
10.52	8.68	4.32	2.82	1.71	0.1M KNO ₃ (25°C)	This work
10.42	8.76	4.42	2.56	1.79	0.1M KNO ₃ (25°C)	13
10.58	8.60	4.27	2.64	1.5	0.1M KCl (20°C)	2
10.55	8.60	4.26	2.41	2.08	0.1M KCl (20°C)	3

TABLE IV

Summary of Stability Constants of Cu-EDTA and Cu-DTPA

<u>log K₀</u>	<u>log K₁</u>	<u>log K₂</u>	<u>log K₃</u>	<u>log A</u>	<u>log B₁</u>	<u>log B₂</u>	<u>log B₃</u>	<u>Conditions</u>	<u>Reference</u>
<i>EDTA</i>									
19.19 ± 0.04 ^{a,b}	12.2	8.0	-	-	3.13	2.0	-	0.1M KClO ₄ , (25°C)	This work
18.79 ± 0.1					3.0	-	-	0.1M KCl (20°C)	1
18.80 ± 0.14	11.54	-				-		0.1M KNO ₃ (20°C)	1
<i>DTPA</i>									
21.45 ± 0.10 ^{a,b}	15.9	10.2	8.5	6.79 ± 0.02 ^{a,c}	4.79	2.88	2.56	0.1M KClO ₄ , (25°C)	This work
21.1	15.5	9.8	-	6.79	4.81	3.04	-	0.1M KNO ₃ (25°C)	4
21.53 ± 0.1	15.69			5.54	4.74			0.1M KCl (20°C)	2
21.03	15.27				4.79			0.1M KCl (20°C)	3

a. ± standard deviation of the mean value.

b. Copper concentrations measured by Orion-1 and Orion-2.

c. Copper concentrations measured by Orion-1, Orion-2, and Radiometer "Selectrode."

TABLE V

Removal of Dependence of HY Constants from CuY K₀ Values

<u>log K₀</u>	<u>pH 3</u>		<u>pH 5</u>		<u>pH 7</u>		<u>Reference</u>
	<u>log α</u>	<u>log K₀/α</u>	<u>log α</u>	<u>log K₀/α</u>	<u>log α</u>	<u>log K₀/α</u>	
<i>EDTA</i>							
19.19	10.68	8.51	6.49	12.70	3.33	15.86	This work
18.80	10.60	8.20	6.45	12.35	3.32	15.48	1
<i>DTPA</i>							
21.45	14.76	6.69	9.28	12.16	5.21	16.24	This work
21.1	14.75	6.35	9.28	11.82	5.19	15.91	4
21.53	14.63	6.90	9.25	12.28	5.19	16.34	2
21.03	14.54	6.49	9.22	11.81	5.16	15.87	3

FIGURE TITLES

- Figure 1. FORMATION CURVES FOR H_n EDTA AND H_n DTPA IN 0.1M KNO_3 AT 25°C
- Figure 2. FORMATION CURVES FOR CuH_n EDTA AND CuH_n DTPA IN 0.1M $KClO_4$ AT 25°C
- Figure 3. RESPONSE OF CUPRIC-SELECTIVE ELECTRODE IN Cu-EDTA AND Cu-DTPA AT THE EQUIVALENCE POINT, AS A FUNCTION OF pH
- Figure 4. CALCULATED K_o FOR Cu-EDTA AND Cu-DTPA AS A FUNCTION OF pH
- Figure 5. OBSERVED AND CALCULATED TITRATION CURVES FOR FORMATION OF CuY

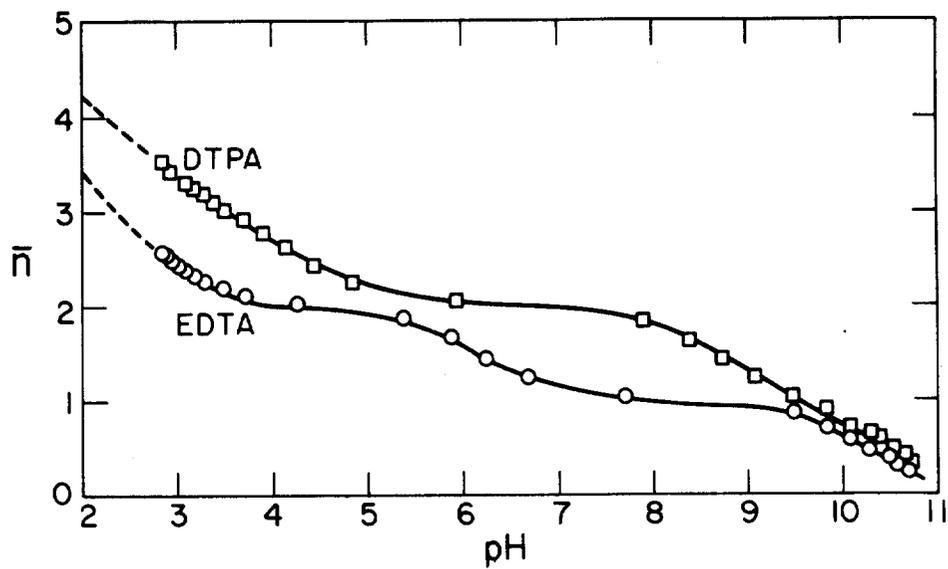


Figure 1. Formation Curves for H_n EDTA and H_n DTPA in 0.1M KNO_3 at 25°C

○ EDTA
 □ DTPA

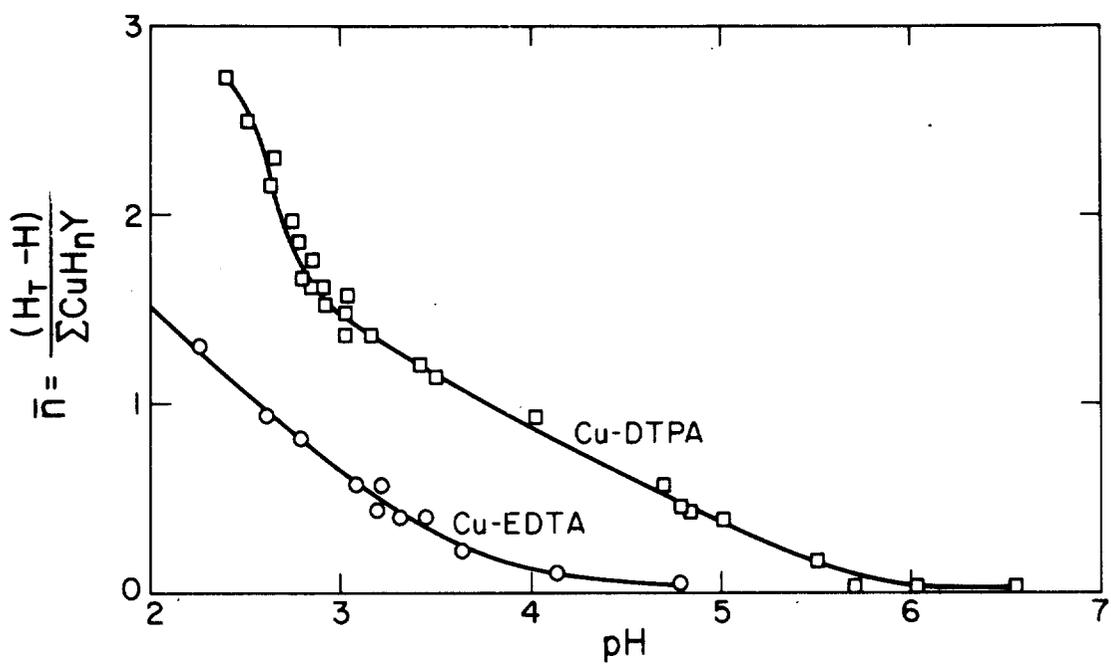


Figure 2. Formation Curves for CuH_n EDTA and CuH_n DTPA in 0.1M $KClO_4$ at 25°C

○ EDTA
 □ DTPA

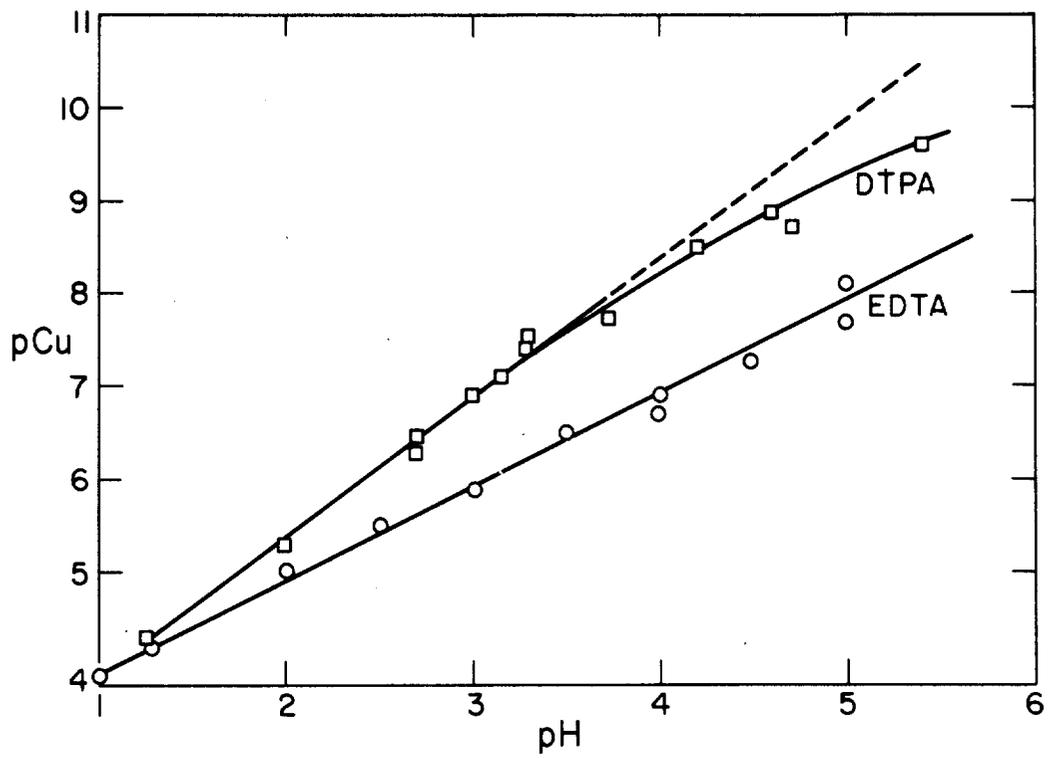


Figure 3. Response of Cupric-Selective Electrode in Cu-EDTA and Cu-DTPA at the Equivalence Point, as a Function of pH

○ EDTA
 □ DTPA

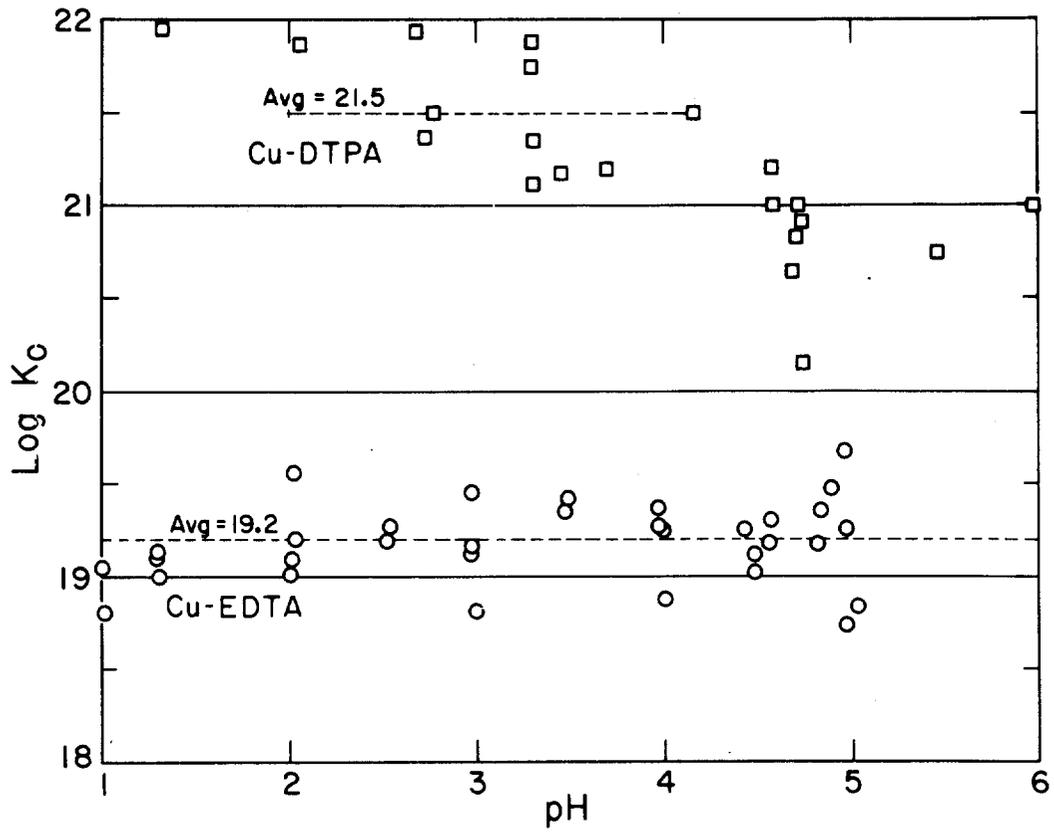


Figure 4. Calculated K_0 for Cu-EDTA and Cu-DTPA as a Function of pH (Orion-2)

○ EDTA
 □ DTPA

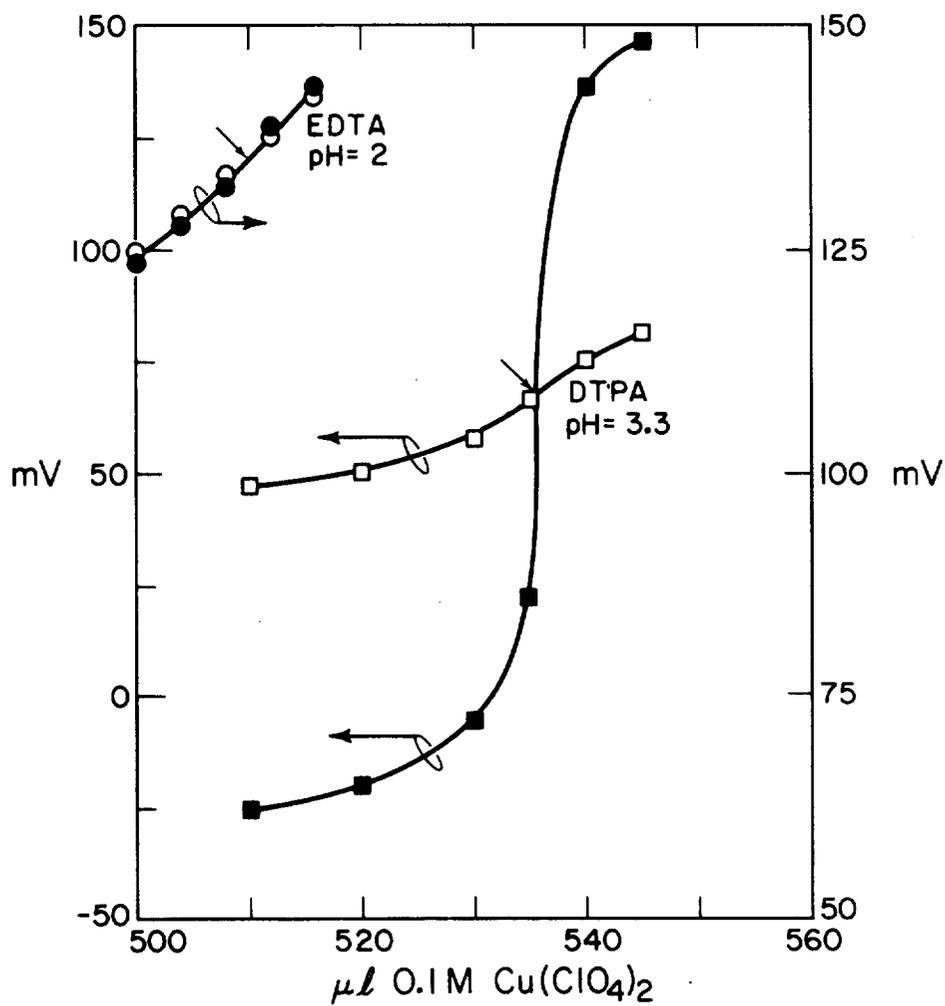


Figure 5. Observed and Calculated Titration Curves for Formation of CuY

○ □ observed

● ■ calculated

→ indicates equivalence point.