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Robert Swann

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THE STEPWISE NATURE OF THE UNWRAPPING AND TRANSFER OF
ETHYLENEDIAMINEDIACETATE FROM NICKEL(II) TO COPPER(II)

by

Robert Swann

A Thesis
Submitted to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
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INTRODUCTION

Multidentate ligand transfer between two metal ions, as represented by equation 1, has been the subject of extensive study for a variety of metal ion combinations and ligands (1, 2, 3, 4, 5, 6, 7, 8, 9).



The mechanism of these reactions has been shown to follow the successive breaking of a series of coordinate bonds from the metal-ligand complex, followed by a stepwise coordination to the attacking metal. This process leads to the formation of a dinuclear intermediate found in all cases where sterically possible (3), followed by breakup to form the products. The stability of each reaction intermediate relative to the reactants can be estimated from the stability constant of the coordinated segments and any electrostatic attraction or repulsion. Further, a change in reactant concentration and hydrogen ion concentration can cause a shift in the rate-determining step (9). Finally, the rate constant for each step can be estimated from the exchange rate constant of the aquo metal ion and the stability constant of the coordinated segment.

The present study was undertaken to establish the mechanism of the reaction between copper (II) and ethylenediaminediacetonickelate (II), abbreviated as NiEDDA.



where $EDDA = HOOCCH_2NHCH_2CH_2NHCH_2COOH$

The study was patterned after the work on copper (II) and ethylenediaminetetraacetate (II) (NiEDTA) (1, 9). From a consideration of the general mechanism for this type of reaction and the similarity of the ligands, it is not at all surprising that the present study fits the mechanism perfectly. Of more importance is the fact that this study is a necessary precursor to the study of an exchange reaction between copper (II) and ethylenedithioglycolate (II), where the only difference is the replacement of the ligand nitrogens by sulfur. This reaction has biochemical significance since metal-ligand exchange reactions can serve as models for metallo-enzyme studies and since very little is known kinetically about biochemically important multidentate ligand reactions with metals.

This study shows that reaction 2 does proceed through a dinuclear intermediate, NiEDDACu, that the rate constant for each step can be estimated from the exchange rate constant of the aquo metal ion and the stability constant of the coordinated segment and that the rate-determining step is dependent upon the initial copper (II) concentration. Comparison of this study with future work involving the sulfur analog of ethylenediaminediacetic acid (EDDA) will yield important information as to metal-sulfur bonding.

APPARATUS AND REAGENTS

Apparatus

All absorbance measurements were made on a Cary Model 14 spectrophotometer with the exception of measurements for the proton study of CuEDDA and NiEDDA, which were made on a Beckman Model B spectrophotometer. The cells were placed in water jacketed cell holders in the Cary Model 14 which maintained temperature constant at $25^{\circ}\text{C} \pm 0.1$

Instrument settings were as follows for all measurements: dynode - 2, slit control - 20, spectral slit width - programmed, varied from .14 to .16, slit height - 20 mm, source - tungsten, chart speed - 1/3 or 1/6 inch per minute. The photometric accuracy was good to ± 0.003 absorbance units and the wavelength calibration accurate to $\pm 0.5\text{ m}\mu$.

All pH measurements were made on a Beckman Research Model pH meter. A glass-calomel electrode pair was used. Sodium chloride was substituted for potassium chloride in the reference electrode to avoid any interference due to potassium perchlorate precipitation.

Reagents

All solutions were prepared using distilled water that had passed through a deionizing column of Amberlite MB-3 mixed bed resin.

Primary Standard Copper Nitrate

Pure copper wire (99.9% pure) was rinsed with dilute nitric acid, water and ethanol, then dried, weighed and dissolved in a minimum amount of concentrated nitric acid. After dilution to volume, the concentration was 0.09754 M.

EDTA

Ethylenediaminetetraacetic acid (EDTA) was obtained in reagent grade from Matheson Coleman Corp. It was purified by two recrystallizations from ethanol and water. It was standardized by titration against a standard copper solution using murexide as the indicator (10).

Copper Perchlorate, Nickel Perchlorate

Standard copper perchlorate and nickel perchlorate solutions were prepared from G. F. Smith copper and nickel perchlorate hexahydrates. Both were standardized by direct titration with EDTA using murexide as the indicator (10).

EDDA

Ethylenediaminediacetic acid was obtained in reagent grade from the K and K Laboratories. It was purified by two recrystallizations with the addition of perchloric acid to a hot basic solution of EDDA followed by cooling. It was standardized by a mole ratio plot against standard copper (II) at 670 mμ and pH 5.0 (Acetic acid, sodium acetate buffer).

CuEDDA, NiEDDA

CuEDDA and NiEDDA solutions were prepared by adding 5% excess copper or nickel solutions to a standard solution of EDDA, followed by the addition of sodium hydroxide to pH 10.5 to precipitate the excess copper or nickel as its hydroxide. The solutions were then filtered through a millipore filter using 0.45 μ paper and adjusted to pH 7 where both complexes exhibit their maximum stability determined from plots of the conditional stability constants against pH.

The NiEDDA solution was standardized spectrophotometrically by both the determination of the nickel content and the absorbance of a solution of the complex. The nickel content was determined at 267 m μ by the addition of a 100-fold excess of potassium cyanide at pH 10 (ammonia-ammonium chloride buffer) to give tetracyanonickelate (II). The molar absorptivity of tetracyanonickelate (II) was determined from a standard nickel perchlorate solution and a 100-fold excess of potassium cyanide at pH 10.

The nickel EDDA solution was also standardized at 670 m μ at pH 4.0. Its molar absorptivity was obtained from a standard NiEDDA solution prepared from standard nickel perchlorate and an excess of EDDA.

The CuEDDA solution was standardized spectrophotometrically at 670 m μ at pH 4.0. Its molar absorptivity was obtained from a standard CuEDDA solution prepared from standard copper perchlorate and an excess of EDDA.

All other chemicals were reagent grade and used without further purification.

EXPERIMENTAL

Spectrophotometric Study of Reactants and Products

The spectra of all reactants and products were obtained from 400 to 800 $m\mu$. Figure 1 shows the absorption spectra. The wavelength of 670 $m\mu$ corresponding to the absorption maximum of CuEDDA was chosen to follow the reaction.

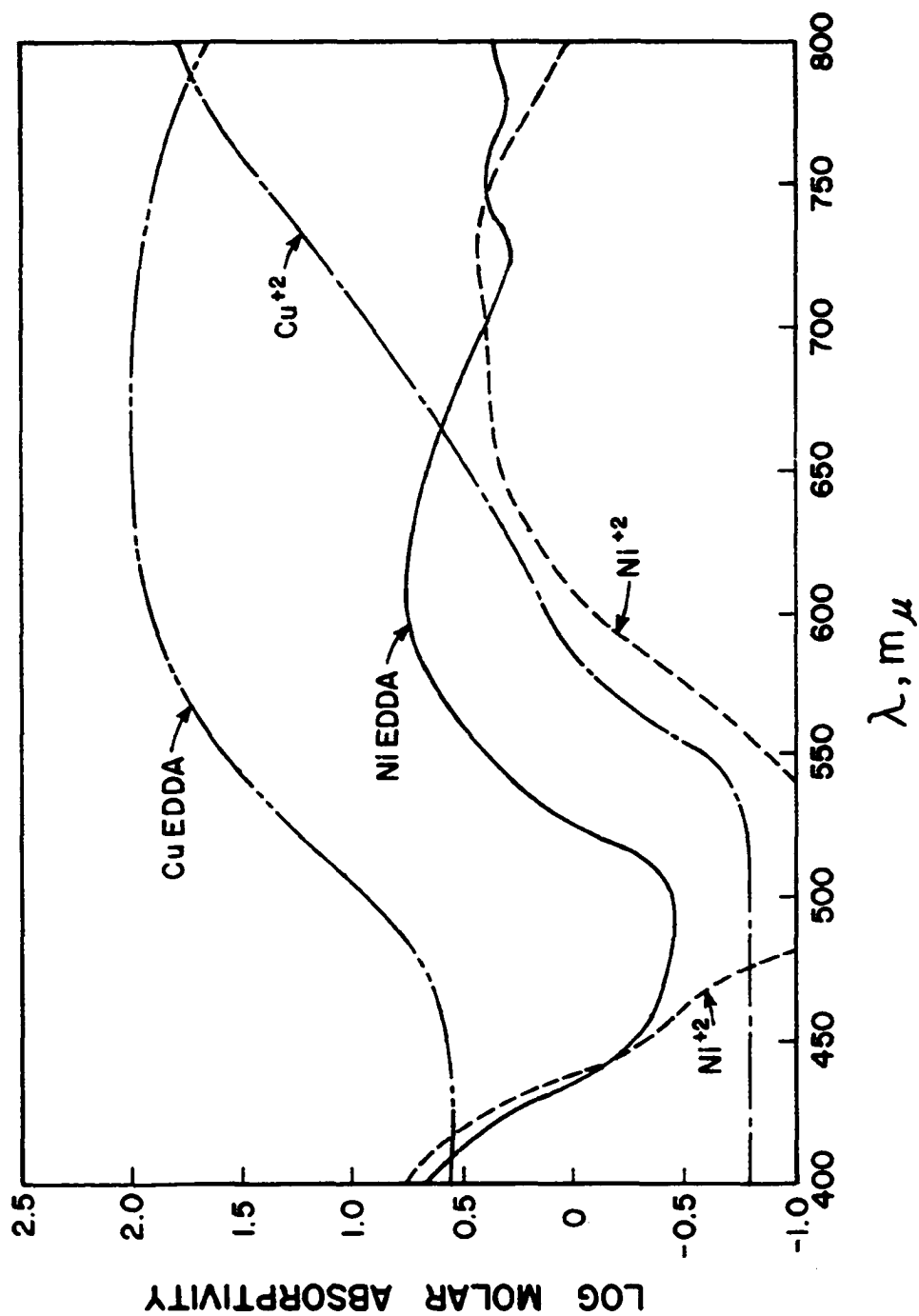


Figure 1. Absorption spectra of reactants and products at pH = 4, $\mu = 1.25$.

The molar absorptivities of copper perchlorate and nickel perchlorate were determined at 670 $m\mu$. Sodium perchlorate was used to adjust the ionic strength to 1.25. The pH was adjusted to 4.00 ± 0.05 using perchloric acid and sodium hydroxide. The values found are listed in Table I.

The molar absorptivities of CuEDDA and NiEDDA were determined at 670 $m\mu$ by measuring the absorbance of a series of solutions containing a constant excess of ligand and varying amounts of standard copper or nickel perchlorate. The ionic strength and pH were adjusted as described above. The EDDA concentration was about ten times greater than the most concentrated metal solution and the values of the conditional stability constants of both complexes predict virtually 100% complexation under these conditions. The absorbance of each solution was then plotted versus the concentration of the complex and the molar absorptivities calculated from the slope of the plot. The values obtained are listed in Table I with the absorbances and concentrations used to get them.

A pH study of CuEDDA and NiEDDA was done spectrophotometrically to see if any protonated forms of either complex existed. The pH was varied from 1 to 5 and the absorbance of the solution measured and plotted versus pH. Table II lists the data and Figures 2 and 3 show the curves obtained. The absorbances below pH 1.0 correspond to that for a solution of the free metal only, thus showing that no protonated species exist and the only change detected was the break up of the complex to form free aquated metal and free ligand. This same conclusion regarding a similar compound was reached in a previous study (11).

TABLE I

Molar Absorptivities at 670 $m\mu$, $\mu = 1.25$, 25.0°C

Metal	Concentration, \underline{M}	Cell length	Abs.	Molar Absorptivity
Ni(II)	4.15×10^{-3}	10	0.090	$2.16 \pm .09$
Cu(II)	4.30×10^{-3}	10	0.188	$4.38 \pm .07$

NiEDDA

Concentration, \underline{M}	Cell length	Absorbance
2.08×10^{-3}	10	.092
3.11×10^{-3}	10	.126
4.14×10^{-3}	10	.145
5.19×10^{-3}	10	.172
6.23×10^{-3}	10	.228

Molar Absorptivity = $3.64 \pm .07$

CuEDDA

Concentration, \underline{M}	Cell length	Absorbance
1.14×10^{-3}	10	.130
2.28×10^{-3}	10	.270
3.41×10^{-3}	10	.388
4.57×10^{-3}	10	.495
5.69×10^{-3}	10	.627

Molar Absorptivity = 111 ± 2

TABLE II

Spectrophotometric pH study of CuEDDA and NiEDDA at 670 $m\mu$

CuEDDA

$$[\text{CuEDDA}] = 4.59 \times 10^{-3} \text{ M}, [\text{Cu}^{+2}] = 1.14 \times 10^{-2} \text{ M}$$

pH	Abs.	pH	Abs.
1.13	.130	2.28	.528
1.20	.152	2.50	.539
1.40	.268	2.65	.550
1.55	.345	2.80	.550
1.69	.425	3.15	.550
1.80	.458	3.23	.550
1.89	.485	3.39	.550
1.98	.506	3.50	.550
2.10	.520	4.09	.550

NiEDDA

$$[\text{NiEDDA}] = 3.90 \times 10^{-3} \text{ M}, [\text{Ni}^{+2}] = 3.80 \times 10^{-2} \text{ M}$$

pH	Abs.
1.00	.450
1.50	.455
1.60	.460
1.80	.490
2.00	.500
3.00	.500
3.50	.500
4.00	.500
4.50	.500

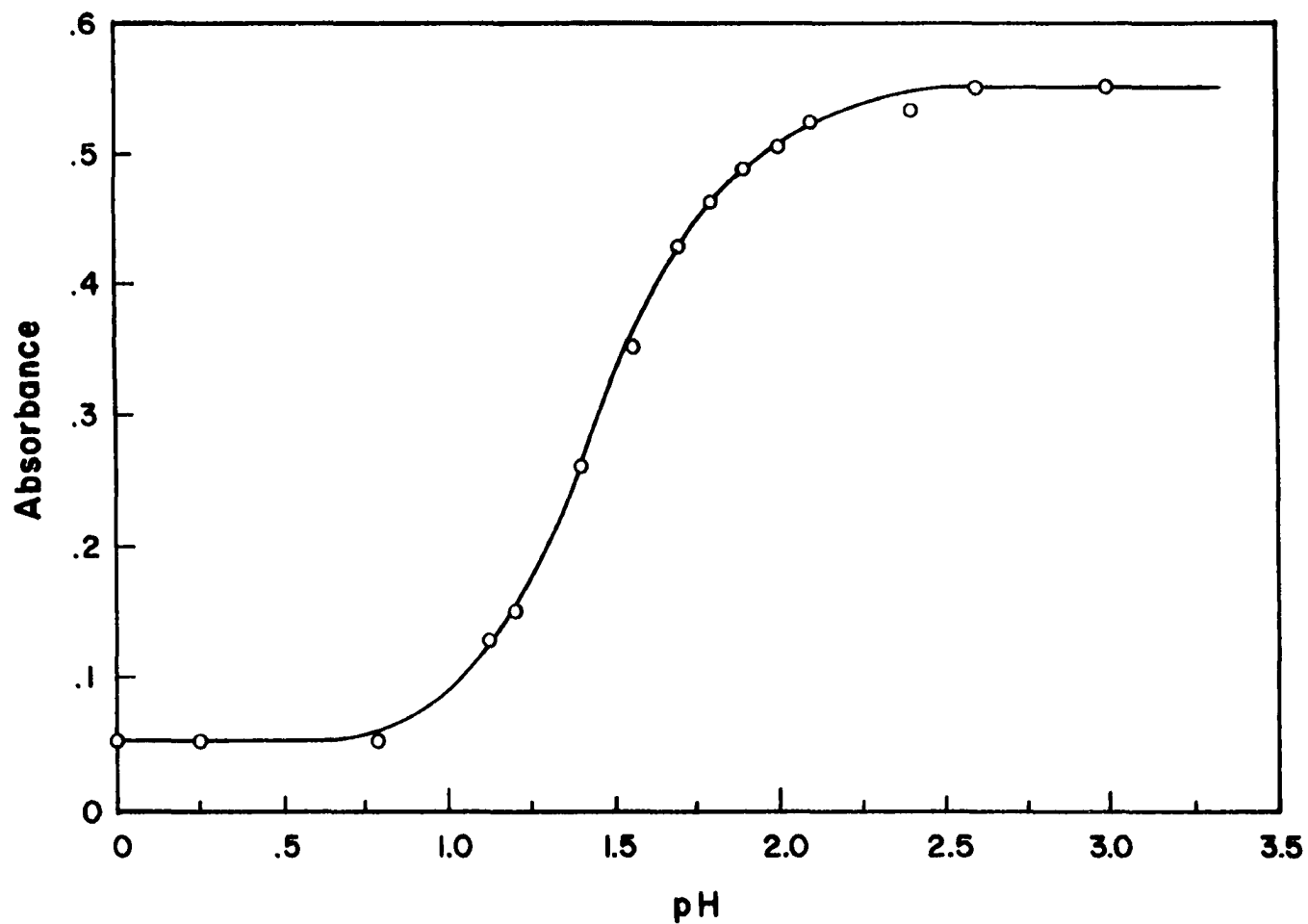


Figure 2. Effect of pH on absorbance of CuEDDA, $\mu = 1.25$, 5 cm cells, $[\text{CuEDDA}] = 4.70 \times 10^{-3} \text{ M}$, excess copper added to repress complete dissociation, $[\text{Cu}^{+2}] = 1.17 \times 10^{-2} \text{ M}$, 670 $m\mu$.

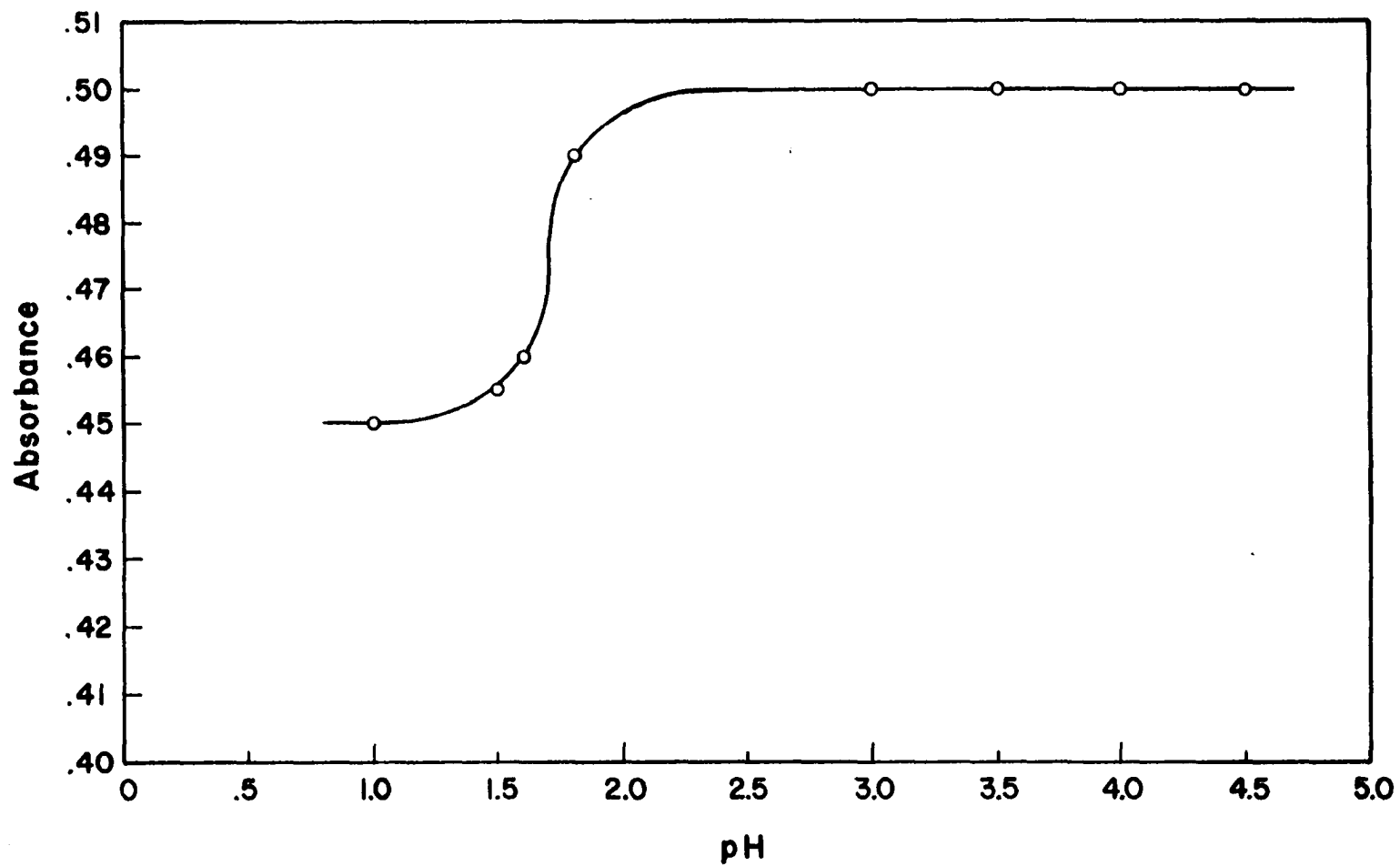


Figure 3. Effect of pH on absorbance of NiEDDA, $\mu = 1.25$, 5 cm cells, $[\text{NiEDDA}] = 3.90 \times 10^{-3} \text{ M}$, excess nickel added to repress complete dissociation, $[\text{Ni}^{+2}] = 1.14 \times 10^{-2} \text{ M}$, 670 m μ .

Reaction Rates and Conditions

All rates of reaction of equation 2 were studied by following the increase in absorbance due to the formation of CuEDDA. Since there is no net change in the number of protons in the reaction (see equation 2), no buffer was necessary. The pH of both reactant solutions was adjusted to the same value with perchloric acid and sodium hydroxide. No difficulty was encountered in maintaining a constant pH. This was demonstrated by mixing reactants and monitoring pH as the reaction proceeded.

In order to compare the rate constants obtained in this study with previous work, the ionic strengths of all reactions was maintained at 1.25 using sodium perchlorate.

A 10 to 50-fold excess of copper over nickel EDDA was present in all cases except where second-order kinetics were desired. Experimental conditions used in all reaction rate studies are given in Table III.

To initiate the reactions, an aliquot of a stock copper solution needed for a reaction was pipetted into a 50 ml beaker. Enough stock sodium perchlorate was added to give 1.25 M upon dilution to 25 ml, along with enough water to bring the volume to 23 ml. The pH of the solution was adjusted while being stirred on a magnetic stirrer. Water was then added to bring the volume to 25 ml. An aliquot of a stock nickel-EDDA solution was pipetted into a 600 ml beaker. Enough stock sodium perchlorate was added to give 1.25 M upon dilution to 250 ml, along with enough water to

TABLE III

Experimental Conditions Used for All Rate Studies

Reactants:	$[\text{NiEDDA}] = 2.92 \times 10^{-4} \text{ M}$ and $[\text{Cu}^{+2}] = 2.88 \times 10^{-4} \text{ F}$ to $1.50 \times 10^{-2} \text{ F}$
Ionic Strength:	NaClO_4 , 1.25 F
pH Range:	3.16 to 4.95
Temperature:	$25.0^\circ \pm .1^\circ \text{ C}$
Wavelength:	670 m
Cell Path Length:	10.0 cm

bring the total volume to 248 ml. The pH was adjusted in the same manner as with the copper solution. Water was then added to bring the total volume to 250 ml. A 25.00 ml aliquot of the NiEDDA solution was pipetted into a 100 ml beaker which had been placed on a magnetic stirrer. The copper solution was then poured into the beaker and the resulting solution mixed for approximately five seconds. The spectrophotometer recorder was turned on at the same time as the mixing of the solution.

The reactions were followed for at least 2 half lives or approximately one hour. Some reactions were followed for 10 half lives to check for any reversibility. None was found.

The rate expression tested by plotting the data is given in equation 3.

$$\frac{-d[\text{NiEDDA}]}{dt} = \frac{d[\text{CuEDDA}]}{dt} = k [\text{NiEDDA}] [\text{Cu}^{+2}] \quad (3)$$

Integration of equation 3 gives

$$\frac{1}{b-a} \log \frac{a(b-x)}{b(a-x)} = kt / 2.303 \quad (4)$$

where a is the initial NiEDDA concentration, b is the initial copper concentration and x is the CuEDDA concentration at any time, t .

The loss of NiEDDA is equal and opposite to the gain of CuEDDA and can be obtained from the change in absorbance as time progresses. Equation 5 can be derived, see Appendix, which relates the concentration of CuEDDA at any time to the final absorbance, A_{∞} , the absorbance at any time t , A_t , the molar absorptivities of reactants and products and the cell path length, b .

$$[\text{NiEDDA}] = \frac{A_t - A_\infty}{b (\epsilon_{\text{NiEDDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{CuEDDA}} - \epsilon_{\text{Ni}})} \quad (5)$$

Excellent second-order plots of equation 4 were obtained thus establishing an overall second-order reaction. The concentrations used and rate constants obtained are listed in Table IV.

In order to check the individual order of each reactant, rates were measured using at least a 10-fold excess of copper over NiEDDA. Assuming a constant copper concentration due to the 10-fold or greater excess copper concentration, integration of equation 3 gives

$$\log [\text{NiEDDA}] = \log [\text{NiEDDA}]_0 - k_o t / 2.303 \quad (6)$$

when $[\text{NiEDDA}]_0$ refers to the initial concentration and k_o is the observed pseudo first-order rate constant,

$$k_o = k [\text{Cu}^{+2}] \quad (7)$$

Excellent first-order plots of equation 6 were obtained with no deviation from linearity, thus establishing a first-order dependence in NiEDDA. Since the overall reaction is second-order, the copper must be first-order also.

The slope of the first-order rate plots times 2.303 is equal to k_o . Plots of k_o versus the copper concentration for a given pH, shown in Figure 4, demonstrates that as the copper concentration was increased, a marked decrease in copper dependency appeared which approached zero-order copper behavior. The data plotted in Figure 4 are given in Table V.

The straight line marked A on the left-hand side of Figure 4 represents equation 7 which is first-order copper behavior. This

TABLE IV

Second-Order Rate Constants Obtained Under the
Following Conditions $\mu = 1.25$, $25.0^{\circ} \pm .1$ pH = 3.64

<u>[NiEDDA]</u>	<u>[CuEDDA]</u>	<u>k, M⁻¹ sec⁻¹</u>
2.88×10^{-4}	6.04×10^{-4}	0.0646
2.88×10^{-4}	6.04×10^{-4}	0.0692

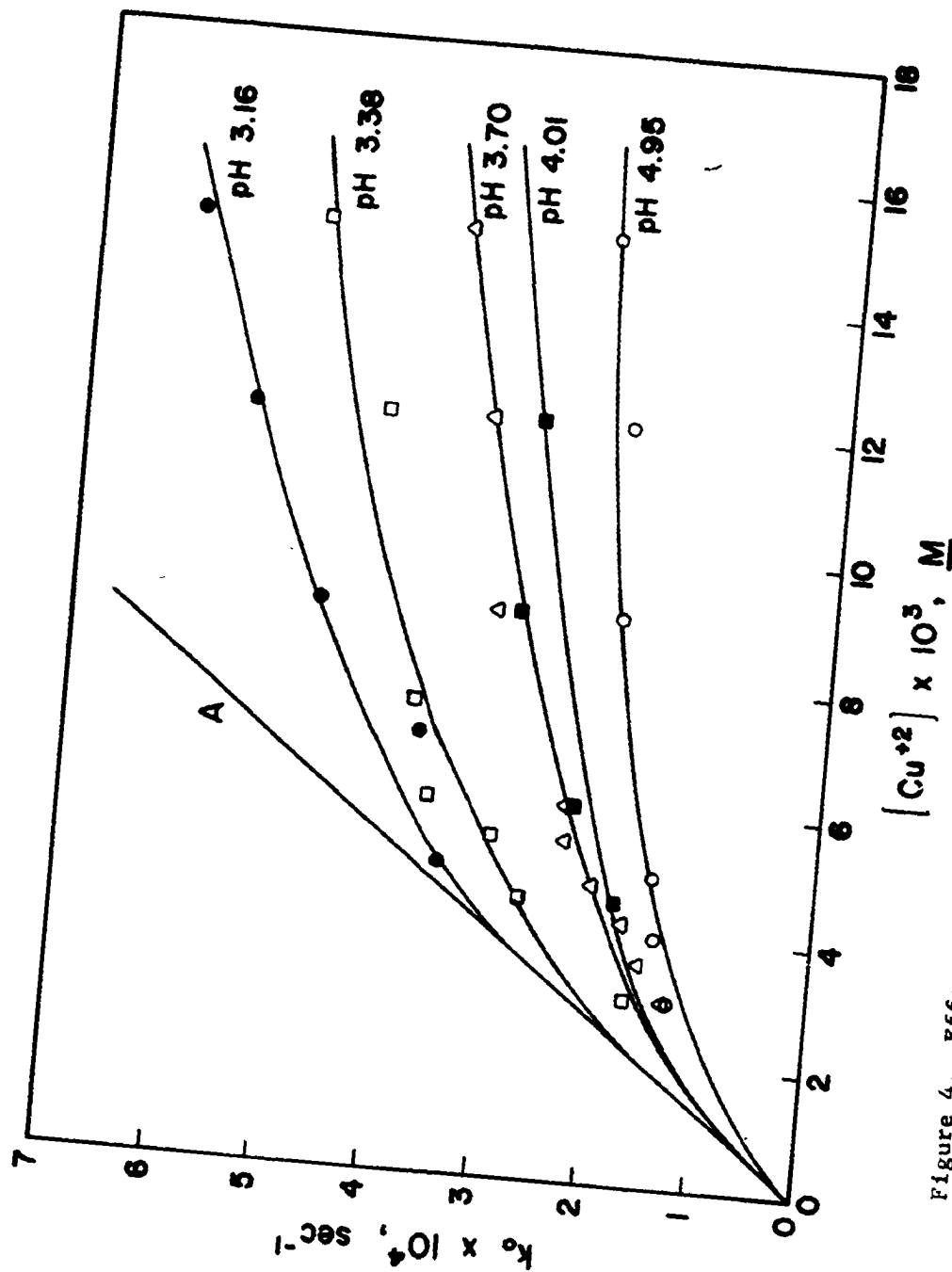


Figure 4. Effect of copper concentration and pH on k_0 . $\mu = 1.25$, 25.0°C .

TABLE V

Effect of pH and Excess Copper Ion Concentration
on Observed First-Order Rate Constant
 $\mu = 1.25, 25.0^\circ$

pH	$[\text{Cu}^{+2}] \times 10^2$	$k_o \times 10^4, \text{sec.}^{-1}$	$[\text{Cu}^{+2}]/k_o, \text{M sec.}$
3.16	0.504	3.44	16.4
	0.706	3.69	19.0
	0.907	4.73	19.0
	1.21	5.46	22.0
	1.51	6.1	24.6
3.38	0.302	1.67	18.0
	0.454	2.68	16.8
	0.544	3.00	18.0
	0.605	3.58	16.8
	0.756	3.78	19.8
	1.21	4.22	29.0
	1.51	4.90	30.6
3.70	0.302	1.35	22.2
	0.383	1.61	23.4
	0.423	1.77	23.8
	0.484	2.07	23.2
	0.544	2.33	23.3
	0.605	2.37	25.3
	0.907	3.08	29.3
	1.21	3.37	35.7
	1.51	3.62	41.5
4.01	0.454	1.85	24.3
	0.605	2.29	26.2
	0.907	2.94	30.4
	1.21	2.86	42.0
4.95	0.302	1.32	22.7
	0.403	1.44	27.8
	0.504	1.53	33.3
	0.907	1.91	47.1
	1.21	2.00	60.0
	1.51	2.26	66.4

linear first-order behavior is approached at low copper concentration. Further, the higher the pH, the lower the concentration of copper needed to cause deviation from the first-order dependency of equation 7.

The data in Figure 4 can be explained as a shift in the rate-determining step from one which occurs after copper attack to one which becomes rate limiting before copper attack as copper is varied from $3.0 \times 10^{-3} \text{ M}$ to $1.5 \times 10^{-2} \text{ M}$. Identical behavior was found in a previous study of NiEDTA and Cu system (9) and equation 8 can be used to separate the two rates involved.

$$k_o = k [\text{Cu}^{+2}] = \frac{a + b [\text{Cu}^{+2}]}{a + b [\text{Cu}^{+2}]} \quad (8)$$

Here, a is the rate constant for zero-order dependence and b is the constant for first-order behavior. At low copper concentration $a > b [\text{Cu}^{+2}]$, and at high copper concentration $b > a [\text{Cu}^{+2}]$.

Rewriting equation 8 as

$$\frac{[\text{Cu}^{+2}]}{k_o} = \frac{1}{b} + \frac{[\text{Cu}^{+2}]}{a} \quad (9)$$

makes it suitable for plotting as shown in Figures 5 through 9 using a least square fit for the data of Table V. The linear relationship found at each pH is in agreement with the transition from first-order to zero-order copper dependence.

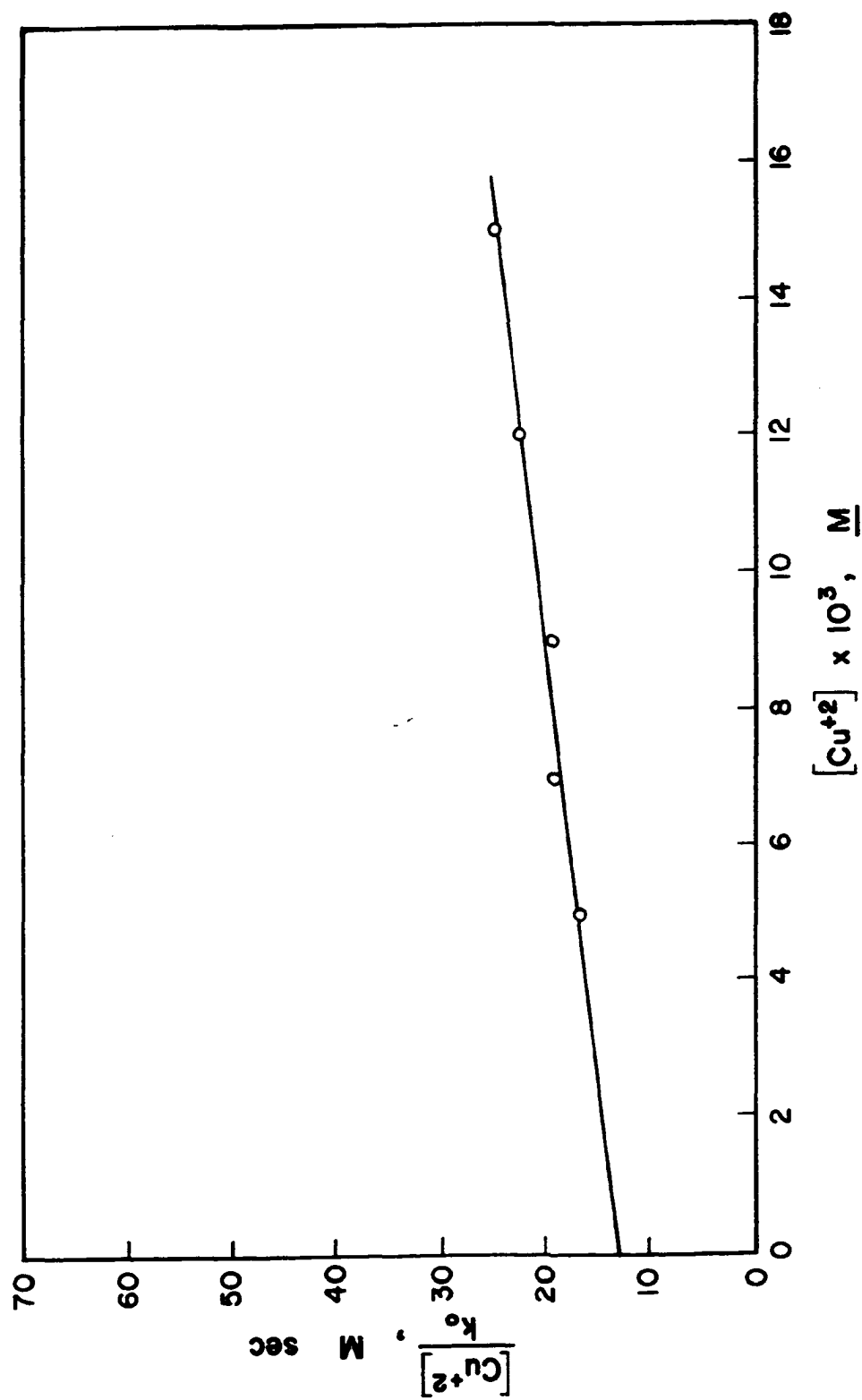


Figure 5. Resolution of k_0 into a and b at $\text{pH} = 3.16$, $\mu = 1.25$.

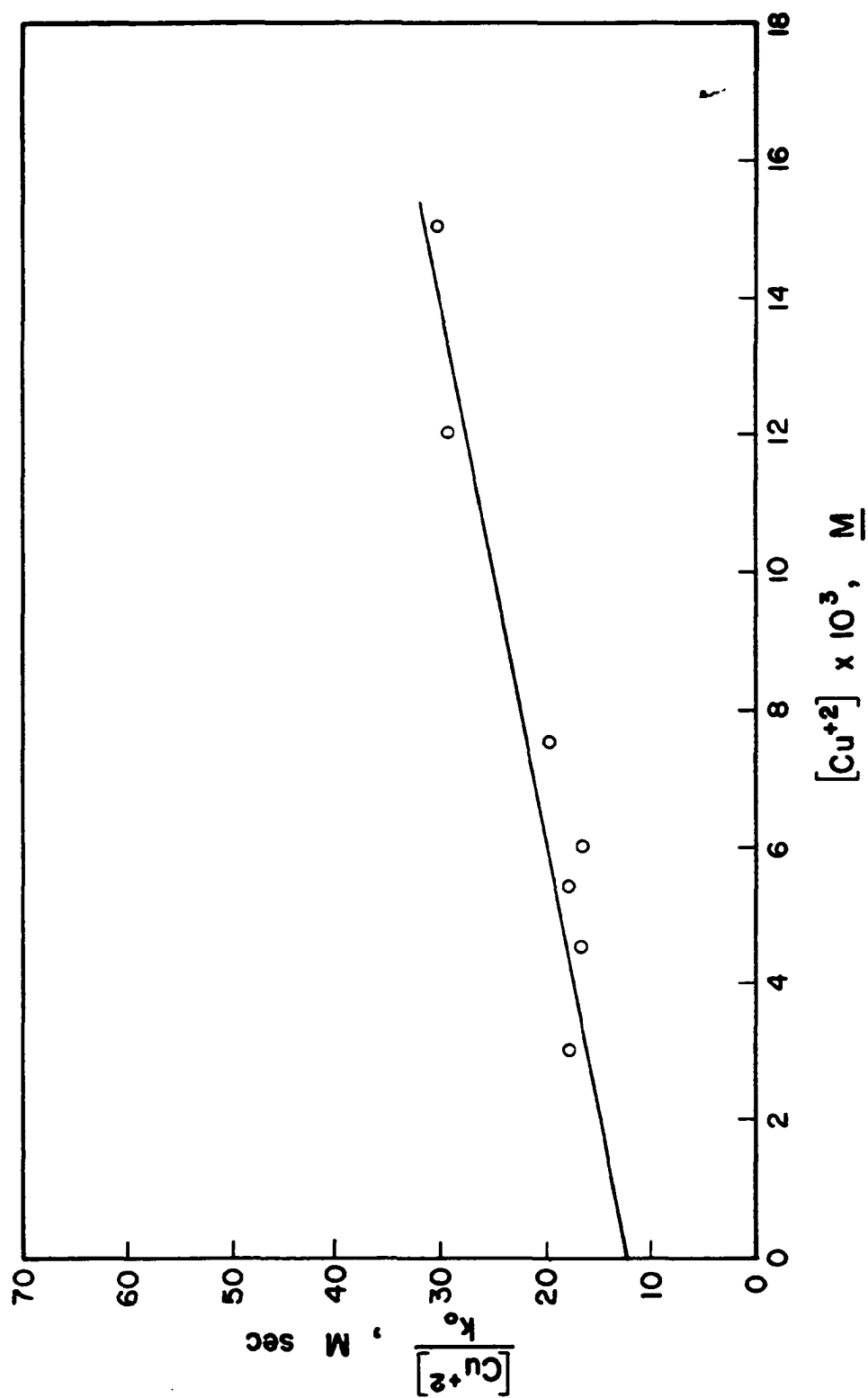


Figure 6. Resolution of k_o into a and b at $pH = 3.38$, $\mu = 1.25$.

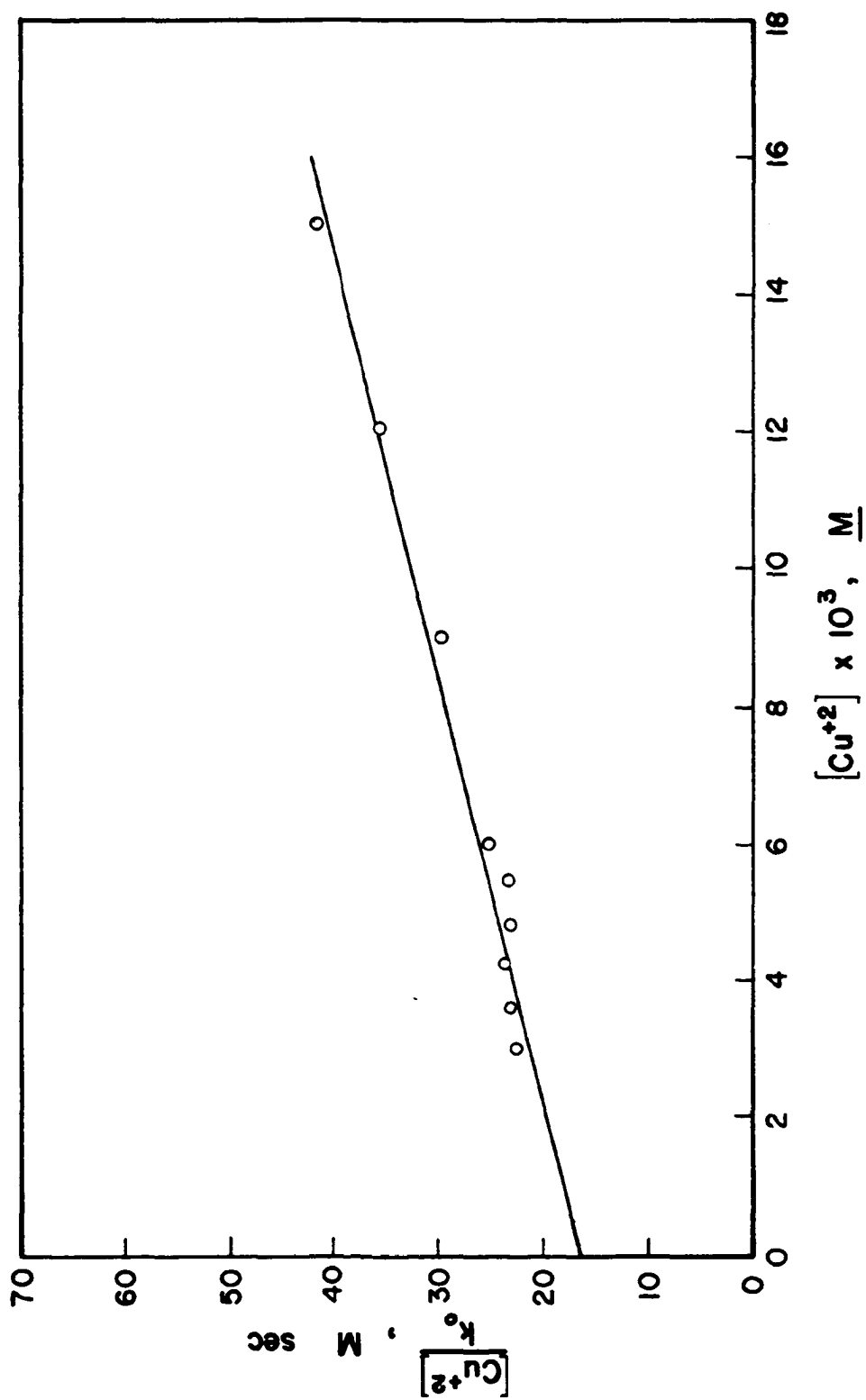


Figure 7. Resolution of k_0 into a and b at $pH = 3.70$, $\mu = 1.25$.

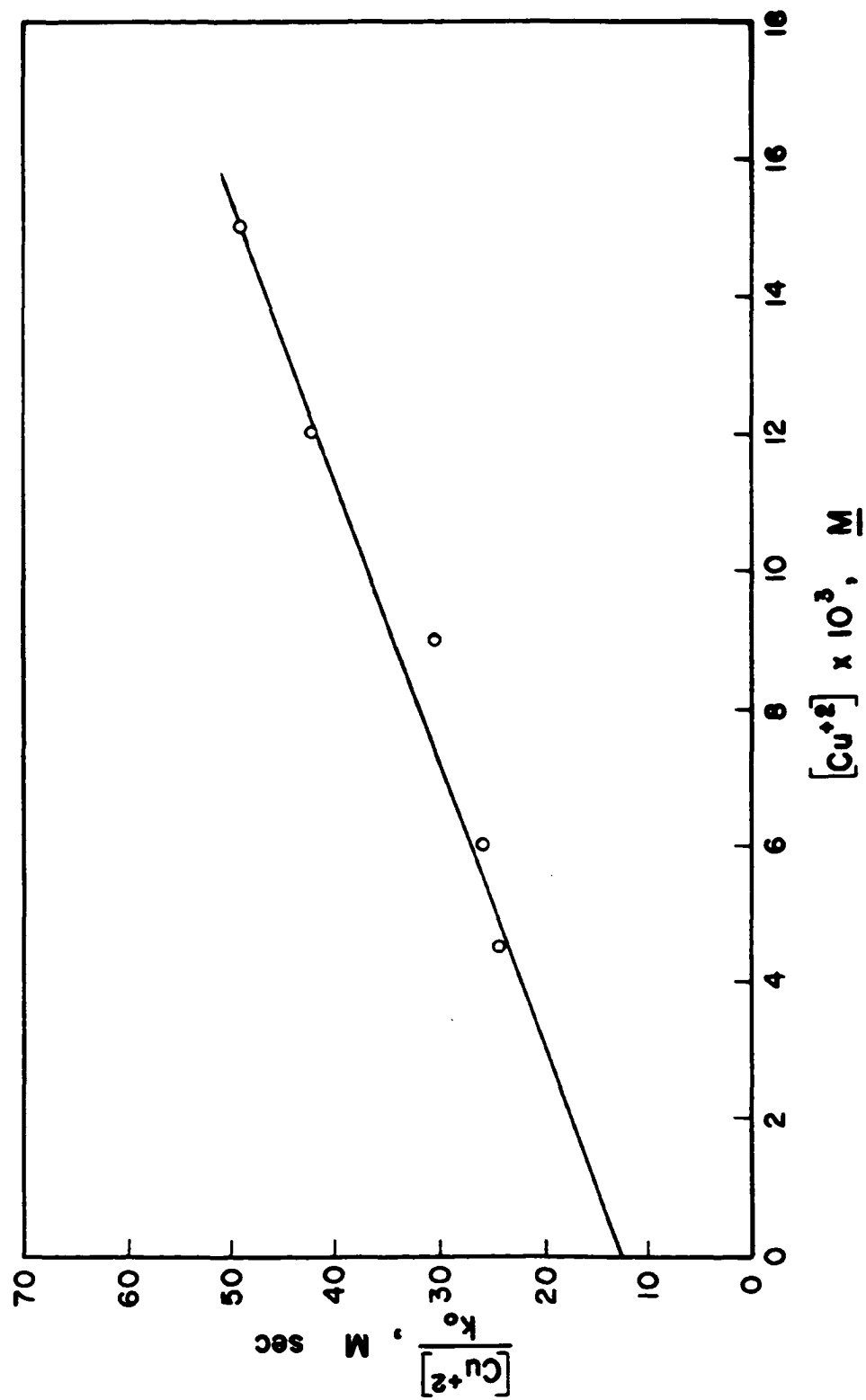


Figure 8. Resolution of k_0 into a and b at $pH = 4.01$, $\mu = 1.25$.

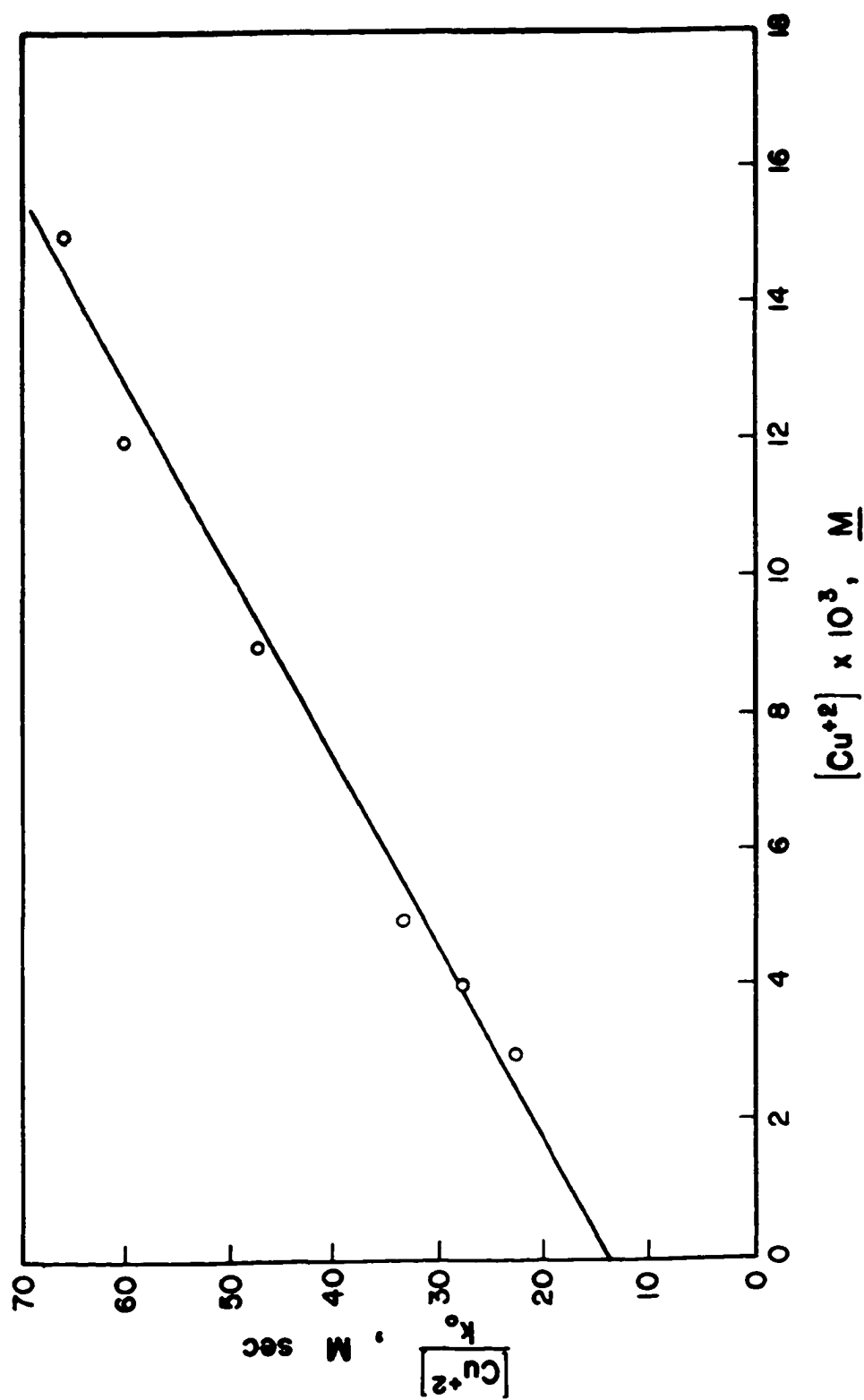


Figure 9. Resolution of k_0 into a and b at $pH = 4.95$, $\mu = 1.25$.

DISCUSSION

Mechanism and General Kinetic Expression

A reaction mechanism is needed to account for the shift in reaction order and the pH sensitivity of the reaction.

A mechanism is outlined in Figure 10 which is consistent with the above points. Protons are omitted from the reaction scheme for the sake of simplicity, although step 1→2 is proton dependent.

The location of the rate-determining step in this mechanism dictates the dependence of the reaction order on copper. However, the great lability of the aquo copper ion means that neither step 2→3 or step 4→5 should be rate determining.

The reaction sequence 1→2→4→5 can easily be ruled out since knowledge of the stability constant of NiEDDA and its rate of formation allow calculation of the rate of reaction along this path. Step 4→5 can not be rate limiting in this sequence as it involves the very labile aquo copper ion as compared to the sluggish dissociation of NiEDDA. Thus the rate for path 1→2→4→5 can be calculated simply from the rate of dissociation of NiEDDA as shown in equation 10.

$$k_{\text{diss}}^{\text{NiEDDA}} = \frac{k_{\text{form}}^{\text{NiEDDA}}}{K_{\text{NiEDDA}}} \quad (10)$$

The conditional stability constant (12) of NiEDDA varies from 7×10^3 to 4×10^7 in the pH range 3.2 to 5.0 and the rate of formation of NiEDDA can be approximated using the rate of formation of NiH_2EDTA .

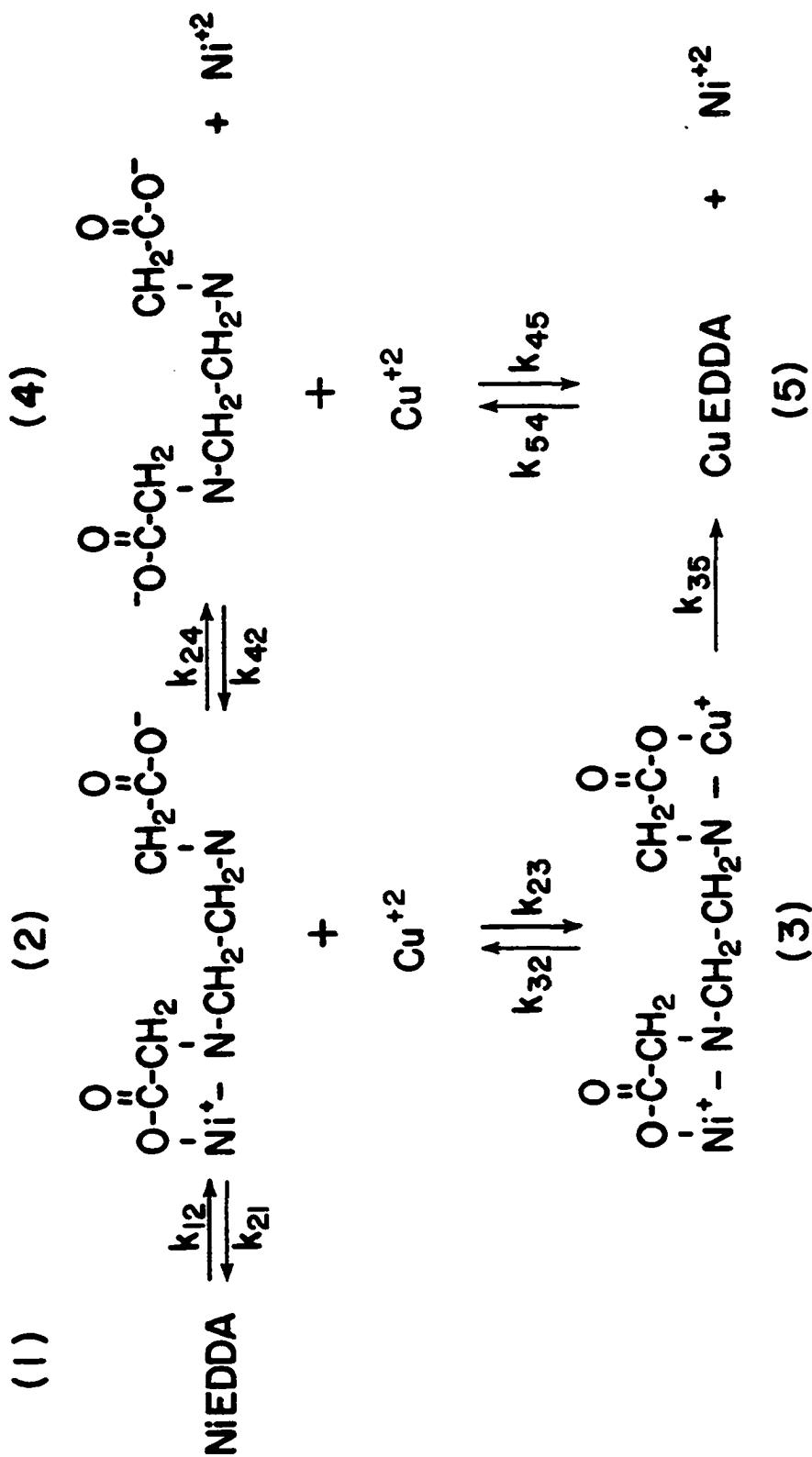


Figure 10. Stepwise transfer of EDDA from nickel to copper.

Formation rate constants for these reactions consist of an outer sphere association constant which depends on charge and metal to ligand distance, and on the rate of water loss of the metal ion. The similarity of EDDA^{-2} and $\text{H}_2\text{EDTA}^{-2}$ as to charge and structure is practically identical. Therefore, $k_{\text{form}}^{\text{NiEDDA}} = 1 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ (13).

From equation 10, $k_{\text{diss}}^{\text{NiEDDA}}$ is calculated to vary from $1.4 \times 10^{-1} \text{ sec}^{-1}$ at pH 3.2 to $1 \times 10^{-4} \text{ sec}^{-1}$ at pH 5.0. Taking the constant hydrogen ion concentration into consideration gives values of the dissociation rate of path $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$ as varying from $8 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ to $1 \times 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$. Thus, this path can be neglected as the calculated rate constants are generally less than those observed at these pH values.

The reaction must therefore proceed through path $1 \rightarrow 2 \rightarrow 3 \rightarrow 5$. Neglecting path $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$ and applying a steady state approximation to species 2 and 3 a general kinetic expression can be derived.

$$\frac{-d [\text{NiEDDA}]}{dt} = \frac{d [\text{CuEDDA}]}{dt} = k_o [\text{NiEDDA}] = k_{35} [3] \quad (11)$$

Writing a steady state approximation for species 2 and 3 gives the following equations:

$$[2] = \frac{k_{12} [\text{NiEDDA}] + k_{32} [3]}{k_{21} + k_{23} [\text{Cu}^{+2}]} \quad (12)$$

$$[3] = \frac{k_{23} [\text{Cu}^{+2}] [2]}{k_{32} + k_{35}} \quad (13)$$

Substituting equation 12 into equation 13 gives

$$[3] = \frac{k_{23} k_{12} [\text{NiEDDA}] [\text{Cu}^{+2}]}{k_{21} k_{32} + k_{21} k_{35} + k_{23} k_{35} [\text{Cu}^{+2}]} \quad (14)$$

Substitution of equation 14 into equation 11 and elimination of

$k_{21} k_{35}$ since k_{35} involves the reaction of sluggish nickel whereas

k_{32} and k_{23} both involve the reaction of labile copper so that

$k_{21} k_{32} > k_{21} k_{35}$ and $k_{23} k_{35} [\text{Cu}^{+2}] > k_{21} k_{35}$ gives

$$\frac{-d [\text{NiEDDA}]}{dt} = \frac{k_{35} k_{23} k_{12} [\text{NiEDDA}] [\text{Cu}^{+2}]}{k_{21} k_{32} + k_{23} k_{35} [\text{Cu}^{+2}]} = k_o [\text{NiEDDA}] \quad (15)$$

Rationale for these approximations are given in the Appendix.

At low copper concentration, $k_{21} k_{32} > k_{23} k_{35} [\text{Cu}^{+2}]$ and equation 15 reduces to

$$k_o = \frac{k_{12} k_{23} k_{35}}{k_{21} k_{32}} [\text{Cu}^{+2}] \quad (16)$$

which shows a first-order copper dependence and, combined with

equation 7, gives a second-order rate constant

$$k_{\text{Cu}}^{\text{NiEDDA}} = \frac{k_{12} k_{23} k_{35}}{k_{21} k_{32}} \quad (17)$$

with the rate determining step as k_{35} .

However, at higher copper concentrations, $k_{23} k_{35} [\text{Cu}^{+2}] > k_{21} k_{32}$ and equation 15 reduces to simply

$$k_o = k_{12} \quad (18)$$

Thus, the reaction at high copper concentration is zero-order in copper and the rate determining step has been shifted to k_{12} .

Rearranging equation 15 gives

$$\frac{[\text{Cu}^{+2}]}{k_0} = \frac{1}{\frac{k_{12} k_{23} k_{35}}{k_{32} k_{21}}} + \frac{[\text{Cu}^{+2}]}{k_{12}} \quad (19)$$

which is the same form as equation 9. Least square plots of equation 9 rewritten as equation 19 are shown in Figures 5 through 9. The intercept of these plots, $1/b$ from equation 9, is $1/k_{\text{Cu}}^{\text{NiEDDA}}$ and the slope, $1/a$ is $1/k_{12}$. The values for these constants at the pH's studied are listed in Table VI.

Step $1 \rightarrow 2$ is proton dependent and copper independent whereas step $2 \rightarrow 3$ is copper dependent and proton independent. Step $1 \rightarrow 2$ in the reaction mechanism corresponds to the unwrapping of a portion of EDDA from nickel. As the copper concentration increases, the relative concentration of species 3 increases and the rate increases. This is easily seen from a rearrangement of the steady state approximation for species 3.

$$\frac{[3]}{[2]} = \frac{k_{23} [\text{Cu}]}{k_{35} + k_{32}} \quad (20)$$

This continues until the reaction progress becomes limited by the rate at which species 2 can be formed. The reaction then no longer increases with an increase in copper. Thus, the rate-determining step shifts from step $3 \rightarrow 5$ to step $1 \rightarrow 2$ as a function of copper concentration. This accounts for the behavior seen in Figure 4 and is consistent with the behavior found in the similar reaction between Cu^{+2} and NiEDTA^{-2} (9).

TABLE VI
Copper Dependent and Copper Independent Rate Constants
as a Function of pH

pH	$k_{\text{Cu}}^{\text{NiEDDA}}, \text{ M}^{-1} \text{ sec}^{-1}$	$k_{12} \times 10^4, \text{ sec}^{-1}$
3.16	0.0788 \pm .0034	12.8 \pm 0.85
3.38	0.0815 \pm .0011	7.90 \pm 0.75
3.70	0.0606 \pm .0027	6.20 \pm 0.30
4.01	0.0792 \pm .0014	4.13 \pm 0.45
4.95	0.0745 \pm .0068	2.72 \pm 0.10

Average $k_{\text{Cu}}^{\text{NiEDDA}} = 0.0749 \pm .0037 \text{ M}^{-1} \text{ sec}^{-1}$

pH Dependency of Half Unwrapping

The value of k_{12} was determined at five pH's and varies with pH. By assuming that k_{12} consists of a first-order and a zero-order term in hydrogen ion for the half unwrapping of NiEDDA, equation 21 can be written which allows resolutions of k_{12} into the two terms by plotting k_{12} versus $[H]$

$$k_{12} = k_d^{\text{NiEDDA} - 1/2} + k_H^{\text{NiEDDA} - 1/2} [H^+] \quad (21)$$

Figure 11 shows the plot of equation 21 using the data from Table VI. The linear relationship found indicates the assumed hydrogen dependency to be correct. Again, analogous behavior is seen for the half unwrapping of NiEDTA⁻² (9). The experimental values of the two constants are $k_d^{\text{NiEDDA} - 1/2} = 2.7 \times 10^{-4} \text{ sec}^{-1}$ and $k_H^{\text{NiEDDA} - 1/2} = 1.4 \text{ M}^{-1} \text{ sec}^{-1}$.

Structure of Half Unwrapped Intermediate

The value of $k_d^{\text{NiEDDA} - 1/2}$ can be predicted from the proposed mechanism in Figure 10. Assuming no hydrogen attack in $k_d^{\text{NiEDDA} - 1/2}$, $k_{12} = k_d^{\text{NiEDDA} - 1/2}$ and k_{21} can be approximated by the rate of water loss of nickel iminodiacetic acid which has been estimated to be $7 \times 10^4 \text{ sec}^{-1}$ (15). The ratio of k_{12}/k_{21} , then equals the stability constant for path 1 \rightarrow 2 which is the ratio of the stability constant for Niglycine (15) and NiEDDA.

An electrostatic attraction of the remote negative charge of the unwrapped glycine segment of NiEDDA for the positive nickel adds stability to the Niglycine intermediate. This additional

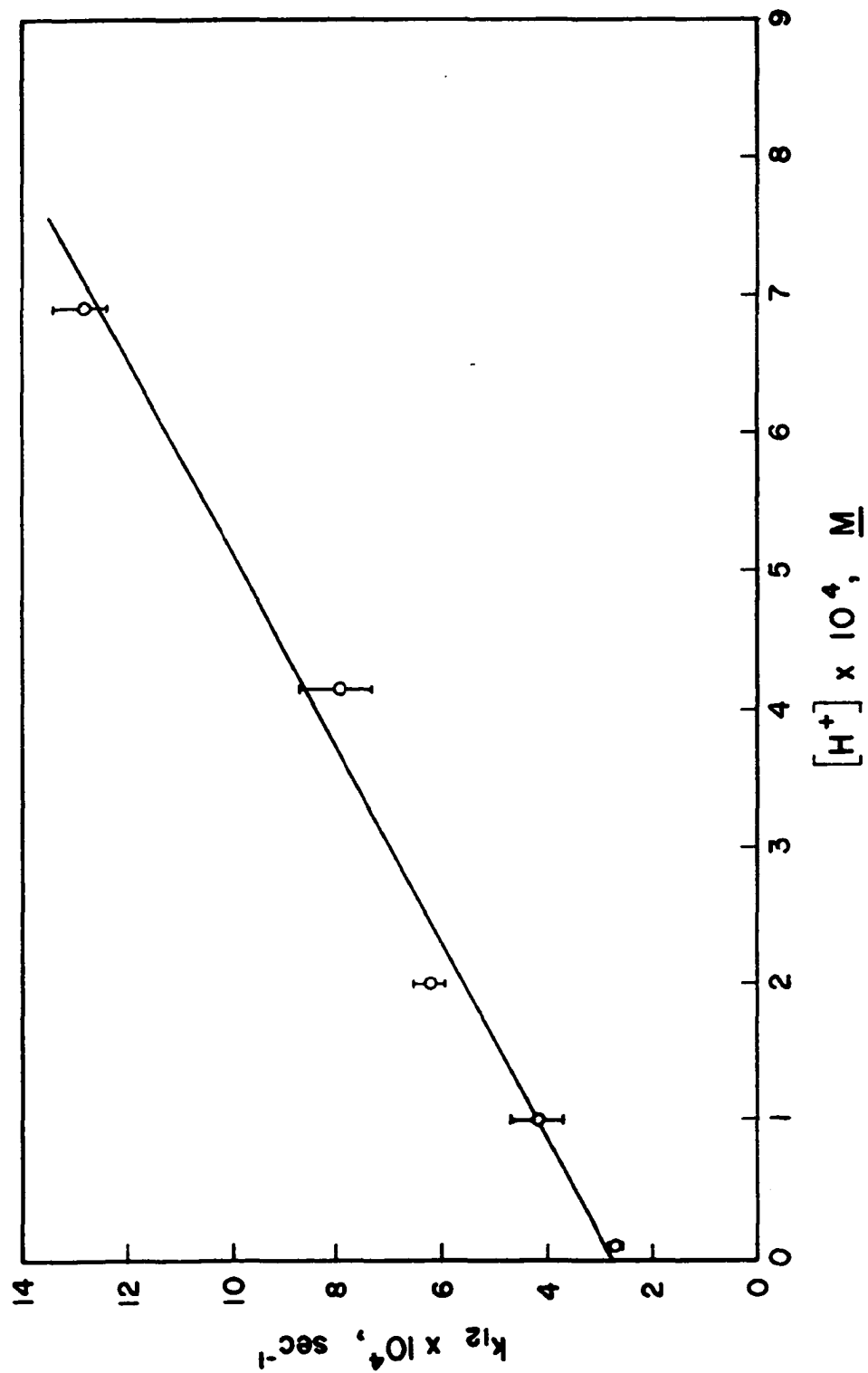


Figure 11. Resolution of k_{12} into proton dependent and proton independent terms. $\mu = 1.25$.

stability can be estimated using equation 22 (3).

$$\Delta E_{\text{electrostatic}} = \frac{z_A z_B e^2}{D r_{AB}} = 2.303 RT \log K_{el} \quad (22)$$

A value of $\log K_{el}$ of 0.45 is obtained from equation 22 using 7A as the charge separation distance (9) and a value of 80 for the dielectric of water.

Also, there is a statistical factor of two favoring the dissociation of NiEDDA. Thus, $k_d^{\text{NiEDDA} - 1/2}$ may be calculated from equation 23.

$$\begin{aligned} k_{12} &= k_d^{\text{NiEDDA} - 1/2} = k_{21} \frac{K_{\text{Ni gly}}}{K_{\text{NiEDDA}}} K_{el} \times 1/2 \quad (23) \\ &= 7 \times 10^4 \text{ sec}^{-1} \times \frac{1.95 \times 10^5}{3.16 \times 10^{13}} \times 2.8 \times 1/2 \\ &= 6 \times 10^{-4} \text{ sec}^{-1} \end{aligned}$$

The predicted value is less than a factor of 3 from the experimentally determined value, which is excellent agreement considering the error shown in Figure 11 and the approximations made. Thus, the structure of species 2, that is the extent of unwrapping of NiEDDA, must be a glycine segment. Either a larger or smaller extent of unwrapping would necessitate the use of a different stability constant in equation 23 which would cause severe disagreement between the predicted and experimental values of k_{12} .

Structure of Dinuclear Intermediate

Further evidence for a glycine segment being unwrapped from NiEDDA may be obtained by considering species 3. The structure of

species 3 can be determined by comparing the experimental ratio of rate constants for metal attack upon various nickel ligand complexes with the ratio of the relative stability constants of the various dinuclear intermediates which form prior to the rate-determining step (3). Previous work (3, 5, 11) has shown that if the bonding to nickel in the intermediate is the same for each set of intermediates compared, the ratio of experimental rate constants is directly proportional to the ratio of intermediate stability constants.

By restricting the bonding to nickel to be identical in each set of intermediates the rate-determining step, corresponding to the breaking of the nickel ligand bonds, k_{35} , is thus the same and cancels out. Equation 24 shows this.

$$\frac{k_{\text{Cu}}^{\text{NiEDDA}}}{k_{\text{M}}^{\text{NiL}}} = \frac{K_{\text{NiEDDA} - \text{Cu}}}{K_{\text{NiL M}}} \frac{\cancel{k_{\text{NiEDDA Cu}}}}{\cancel{k_{\text{NiL M}}}} \quad (24)$$

Since the ratio of the intermediate stability constants are used, it is more convenient to use relative values for these constants. The relative stability constant, K_R , of each structure can be defined in terms of the stability constant of the CuEDDA and NiEDDA segments of the dinuclear intermediate, compared to the stability constant of the initial complex.

$$K_R = \frac{K_{\text{Cu segment}} K_{\text{Ni segment}}}{K_{\text{Ni complex}}} \quad (25)$$

In some intermediate comparisons, an electrostatic attraction helps to stabilize one structure relative to the other. This

additional stability can be estimated using equation 22, with a value of 6A as the charge separation distance, r_{ab} (3), and a value of 80 for the dielectric constant of water. In comparing the intermediates NiEDDA Cu to NiEDTA Cu, there is a net attraction of the unbound acetate group, for the nickel glycinate group which does not exist in the NiEDDA Cu structure. A value of $\log K_{e1} = 0.5$ is obtained for this case.

Further, the formation of some intermediates are favored statistically, over the formation of others. For example, in comparing NiEDTA Cu to NiEDDA Cu, the intermediate involving a glycine segment of EDTA bonded to nickel and an iminodiacetate segment bonded to copper can be formed in four independent ways whereas an intermediate involving a glycine segment of EDDA bonded to nickel and a glycine segment bonded to copper can only form in two independent ways.

The intermediate structures compared, the K_R values, and electrostatic and statistical factors where needed are given in Table VII. A comparison of the ratio of relative stability constants for the dinuclear intermediates with the ratio of experimental rate constants gives excellent agreement. Other possible intermediates gave K_R values which were either very high or very low. Thus, the intermediate which exists in the NiEDDA, copper system involves a glycine segment bonded to copper and a glycine segment bonded to nickel.

The rate-determining step, k_{35} , is actually the breaking of the nickel-nitrogen bond since nickel acetate bonds cleave at

TABLE VII
Comparison of NiEDDA Cu and NiL M Reaction Intermediates

NiEDDA Cu	NiL M	Predicted Ratio $K_{\text{NiEDDA}} / K_{\text{NiL Cu}}$	Experimental Ratio $k_{\text{Cu}}^{\text{NiEDDA}} / k_{\text{M}}^{\text{NiL}}$
	NiEDTA Cu		
$+ \text{Ni} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{Cu}^+$ $K_R = 2.24 \times 10^{-1}$	$+ \text{Ni} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{Cu}$ $K_R = 1.52 \times 10^{-2}$ $K_{\text{el}} = 3.16$ Statistical factor of 2	5.4	4.7
	NiHEEDTA Cu		
$+ \text{Ni} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{Cu}^+$ $K_R = 2.24 \times 10^{-1}$ Statistical factor of 2	$+ \text{Ni} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{Cu}$ $K_R = 2.40 \times 10^{-1}$	1.9	5.0
	NiEDTA Zn		
$+ \text{Ni} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{Cu}^+$ $K_R = 2.24 \times 10^{-1}$	$+ \text{Ni} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{N} - \text{N} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{Zn}$ $K_R = 5.75 \times 10^{-7}$ $K_{\text{el}} = 3.16$ Statistical factor of 2	6.2×10^4	3.0×10^4

TABLE VII (continued)

K_R values are based on the following stability constants chosen from ref. 15 to be as internally consistent as possible with respect to temperature and ionic strength. The experimental ratio of rate constants are based on the following values, all at $25.0^\circ \pm .1$ and $\mu = 1.25$

Complex	log K	M	L	$k_m^{NiL}, M^{-1} sec^{-1}$	Ref.
NiEDDA	3.16×10^{13}	Cu	EDOA	7.5×10^{-2}	this work
NiEDTA ⁻²	3.63×10^{13}	Cu	EDTA	1.6×10^{-2}	1
NiHEEDTA ⁻	1.00×10^{17}	Cu	HEEDTA	1.5×10^{-2}	3
Ni (glycinate) ⁺	1.95×10^5	Zn	EDTA	2.5×10^{-6}	2
Cu (glycinate) ⁺	3.63×10^7				
Cu (iminodiacetate)	1.23×10^{11}				
Zn (iminodiacetate)	1.07×10^7				

$>2 \times 10^3 \text{ sec}^{-1}$ (3) while nickel-nitrogen bonds cleave at 5.8 sec^{-1} (16). The value of $2 \times 10^3 \text{ sec}^{-1}$ in conjunction with the K_R value of the NiEDDA Cu intermediate greatly exceeds the experimentally observed rate constant. Thus, nickel-nitrogen bond breakage is rate-determining. This is identical with the NiEDTA, Cu system (3, 9).

APPENDIX

The relationship shown in equation 5 between [NiEDDA] and the absorbance at any time, A_t , the final absorbance, A_{∞} , and the molar absorptivities of reactants and products is derived as follows. Assuming no stable intermediate to be present which was shown by spectral scans of the reaction, the absorbance at any time is equal to the absorbance of the reactants left and the products formed. Beers law is assumed to hold and equation 26 can be written.

$$A_t = \epsilon_{\text{NiEDDA}} b[\text{NiEDDA}] + \epsilon_{\text{Cu}} b[\text{Cu}^{+2}] = \epsilon_{\text{Ni}} b[\text{Ni}^{+2}] + \epsilon_{\text{CuEDDA}} b[\text{CuEDDA}] \quad (26)$$

Writing $[\text{Cu}^{+2}]$ as $([\text{Cu}^{+2}]_{\text{final}} + [\text{NiEDDA}])$, $[\text{Ni}^{+2}]$ or $([\text{Ni}^{+2}]_{\text{final}} - [\text{NiEDDA}])$ and $[\text{CuEDDA}]$ as $([\text{CuEDDA}]_{\text{final}} - [\text{NiEDDA}])$, substitution of these expressions into equation 26 and rearranging, equation 27 results.

$$A_t = [\text{NiEDDA}] b (\epsilon_{\text{NiEDDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{Ni}} - \epsilon_{\text{CuEDDA}}) + \epsilon_{\text{Cu}} b[\text{Cu}^{+2}]_{\text{final}} + \epsilon_{\text{Ni}} b[\text{Ni}^{+2}]_{\text{final}} + \epsilon_{\text{CuEDDA}} b[\text{CuEDDA}]_{\text{final}}$$

Since

$$A_{\infty} = \epsilon_{\text{CuEDDA}} b[\text{CuEDDA}]_{\text{final}} + \epsilon_{\text{Ni}} b[\text{Ni}^{+2}]_{\text{final}} + \epsilon_{\text{Cu}} b[\text{Cu}^{+2}]_{\text{final}} \quad (28)$$

substitution of equation 28 into 27 followed by rearrangement yields

$$[\text{NiEDDA}] = \frac{A_t - A_{\infty}}{b (\epsilon_{\text{NiEDDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{CuEDDA}} - \epsilon_{\text{Ni}})} \quad (5)$$

The relative magnitude of $k_{21} k_{35}$, $k_{23} k_{35} [\text{Cu}^{+2}]$ and $k_{21} k_{32}$, resulting in elimination of $k_{21} k_{35}$ in equation 14, can be estimated as follows. The ratio k_{32} to k_{35} can be estimated from the stability constants of Ni glycine and Cu glycine and the rates of water loss of Ni^{+2} and Cu^{+2} .

$$K_{\text{Cu glycine}} = \frac{k^{\text{Cu} - \text{H}_2\text{O}}}{k_{32}} \quad (29)$$

$$K_{\text{Ni glycine}} = \frac{k^{\text{Ni} - \text{H}_2\text{O}}}{k_{35}} \quad (30)$$

$$\frac{k_{32}}{k_{35}} = \frac{K_{\text{Ni glycine}} k^{\text{Cu} - \text{H}_2\text{O}}}{K_{\text{Cu glycine}} k^{\text{Ni} - \text{H}_2\text{O}}} \quad (31)$$

Using the stability constants from Table VII, a value of $7 \times 10^7 \text{ sec}^{-1}$ for $k^{\text{Ni} - \text{H}_2\text{O}}$ (14) and $3 \times 10^8 \text{ sec}^{-1}$ for $k^{\text{Cu} - \text{H}_2\text{O}}$ (17) in equation 31 gives the ratio of k_{32}/k_{35} equal to 24. Thus $k_{21} k_{32}$ is 24 times larger than $k_{21} k_{35}$.

The term $k_{23} k_{35} [\text{Cu}^{+2}]$ is larger than $k_{21} k_{35}$ at high copper concentration but disappears along with $k_{21} k_{35}$ when compared to $k_{21} k_{32}$ at low copper concentration. Since k_{23} involves the rate of water loss of copper, $3 \times 10^8 \text{ sec}^{-1}$, whereas k_{21} is the rate of water loss of nickel, $7 \times 10^4 \text{ sec}^{-1}$, $k_{23} [\text{Cu}^{+2}]$ at low copper, $< 1 \times 10^{-4} \text{ M}$, which was approached experimentally, is less than k_{21} , thus $k_{23} k_{35} [\text{Cu}^{+2}]$ is ignored. At high copper, $> 1 \times 10^{-2} \text{ M}$, which was also approached experimentally, $k_{23} [\text{Cu}^{+2}]$ is greater than k_{21} , thus $k_{21} k_{35}$ may be ignored.

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VITA

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