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Kinetics of the Formation of Nickel(II) Complexes with N,N'-Dibenzylethylenediamine and N,N'-Bis(2-Picolyl)Ethylenediamine

Zahid Amjad

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KINETICS OF THE FORMATION OF NICKEL(II) COMPLEXES
WITH N,N'-DIBENZYLETHYLENEDIAMINE AND
N,N'-BIS(2-PICOLYL)ETHYLENEDIAMINE

by

Zahid Amjad

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
August 1972

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Zahid Amjad

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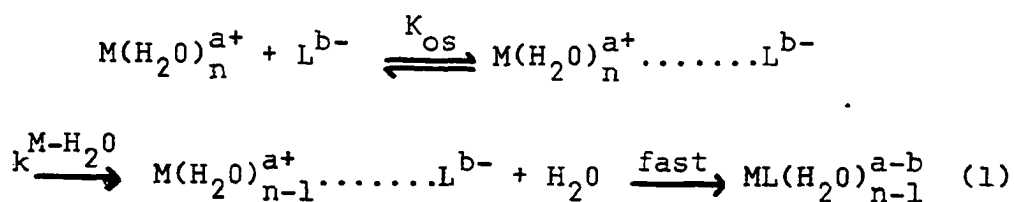
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INTRODUCTION

The replacement of one ligand coordinated to a metal center by another ligand in solution is a fundamental process which permeates all aspects of coordination chemistry. The substitution of a coordinated solvent molecule, usually water, by another complexing molecule is the basis of the formation of metal complexes, while the reverse process is variously referred to as hydrolysis, aquation, or dissociation.

In recent years a large number of kinetic studies have been carried out on the reactions of aquometal ions with both unidentate and multidentate ligands. Nearly all such studies report adherence to the general dissociative mechanism formulated by Eigen (1) as represented by the scheme



In this mechanism $\text{M(H}_2\text{O)}_n^{a+}$ represents an aquometal ion; L^{b-} , a ligand; K_{os} , the diffusion controlled equilibrium constant for the formation of an outer-sphere complex,

$M(H_2O)_n^{a+} \dots \dots L^{b-}$ (a species in which the reactants are the nearest neighbors); and k^{M-H_2O} , the rate constant for metal-water bond rupture. Steps following the first loss of a coordinated water molecule from the metal ion in the outer-sphere complex are usually rapid so that the first such metal-water bond rupture represents the rate-determining step, even for reactions of multidentate ligands which involve subsequent bonding steps (2). For these cases, the formation rate constant, k_M^L , for the observed second-order rate equation

$$-\frac{d[M(H_2O)_n^{a+}]}{dt} = k_M^L [M(H_2O)_n^{a+}] [L^{b-}] \quad (2)$$

can be expressed as

$$k_M^L = K_{OS} k^{M-H_2O} \quad (3)$$

Since K_{OS} can be calculated (2,3) with fair accuracy (4,5) from diffusion equations and k^{M-H_2O} values have been determined independently from temperature jump, (1,6,7) sound absorption (1) and nuclear magnetic resonance measurements (1,8), values for k_M^L can, in many instances, be approximated from a priori calculations using equation 3. In this manner comparison can be made between theoretical and experimental rate constants as a test for the applicability of the dissociative mechanism. The constancy of formation rate con-

stants for reactions involving a series of ligands of the same charge reacting with a specific aquometal ion also serves to support this mechanism (1,2,9).

Although exceptions to the kinetic rates predicted by equation 3 are rare, a few anomalous systems have been noted. In earlier work it was found that the rate constants for the formation of nickel-polyamine complexes markedly exceed the theoretical values. An internal conjugate base (ICB) mechanism dependent on the highly basic nature of the donor atoms, has been proposed to account for the increase in these formation rate constants (6).

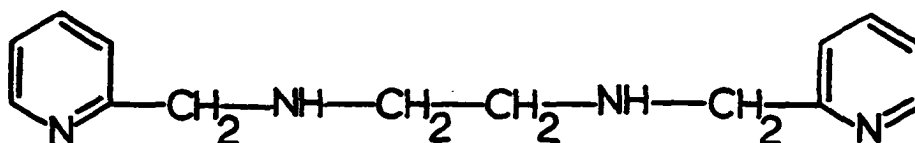
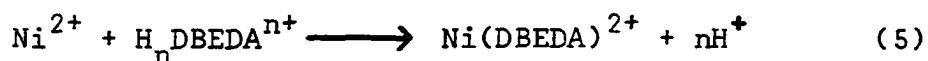
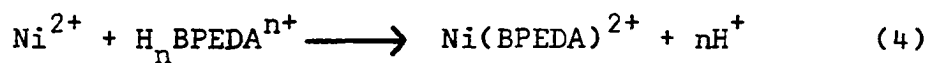
Recent studies have demonstrated other subtle effects in the formation process arising from variations in the ligands which replace coordinated water of the metal ion.

Rorabacher has recently studied the kinetics of Ni(II) reacting with a series of N-alkyl substituted monoamines (10) and N and N,N'-alkyl substituted ethylenediamines (11). From these studies a consistent trend emerges of decreasing nitrogen donor atom reactivity with increasing substitution.

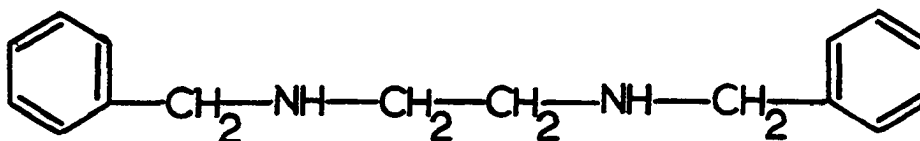
The presence of several types of dentate sites on a single ligand may influence which dentate site is involved in the rate-determining step. The strength of the first metal-ligand bond is important since labile

bonds rupture quickly thus causing subsequent metal bonds to a different type of dentate site to be rate determining. This process, called sterically controlled substitution, has been useful in explaining the reaction of nickel with ethylenediaminetetracetic acid (EDTA), N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylenediamine (TKED), N,N,N',N',-tetrakis (2-hydroxypropyl)ethylenediamine (THPED)(12), and acetylacetone (13).

No work has been reported on the effect which both aliphatic and aromatic dentate sites in a single ligand have on the formation rate. The present study was undertaken to investigate the mechanism of nickel complex formation in the reaction of Ni(II) with ligands containing both aliphatic and aromatic nitrogens. The reactions chosen are shown in equations 4 and 5, and involve Ni(II) and N,N'-bis(2-picoly)ethylenediamine (Structure I) and N,N'-dibenzylethylenediamine (Structure II) abbreviated as BPEDA and DBEDA respectively.



Structure I



Structure II

The kinetic study of these reactions was designed so as to determine whether the first bond formation of Ni(II) takes place with an aliphatic or aromatic nitrogen. From previous studies, both ICB and steric effects were anticipated for these reactions.

This study will attempt to show (i) that reactions 4 and 5 proceed by the Eigen mechanism, (ii) which dentate site is involved in the rate-determining step, (iii) the sequence of bond formation, the presence or absence of the ICB effect and (iv) the magnitude of the steric effects of the various nitrogens present in BPEDA and DBEDA.

Comparison will be made of this study with other work on the kinetics of formation and dissociation of Ni(II) with a variety of ligands analogous to BPEDA and DBEDA containing various combinations of aliphatic and aromatic nitrogens. The effect of substituents on these ligands will also yield important information about the role of steric hinderance and the ICB effect in predicting formation rates.

APPARATUS AND REAGENTS

Apparatus

All pH measurements were made on a Beckman Research Model 1019 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.

A Precision Scientific electronic relay was used to control a constant temperature bath for the kinetic measurements. This maintained the temperature at $25 \pm .1^\circ \text{C}$.

The kinetic measurements were made using an Aminco Morrow stopped-flow mixing chamber attached to a Shimadzu QV50 spectrophotometer. The voltage output was fed to a Tektronix Storage Oscilloscope Type 549 and traces of voltage, calibrated as %T, vs. time, were recorded using a C12 Oscilloscope Camera and Polaroid film.

Other absorbance measurements were recorded using a Cary Model 14 Spectrophotometer with the following instrument setting: source, hydrogen and tungsten lamp; chart speed, 1 and 2 inch per minute; cell path length, 1.0 cm and 10 cm; slit control, 20.

Reagents

All chemicals were reagent grade unless otherwise specified. All solutions were made with deionized water prepared by passing distilled water through a mixed bed ion-exchange column (Amberlite MB-3).

Standard copper(II) nitrate

Pure copper wire (99.90%), Allied Chemical Co., was rinsed with dilute nitric acid, water and ethanol, then dried, weighed and dissolved in a minimum amount of concentrated nitric acid. After diluting to volume, the concentration was 0.1012M.

Ethylenediaminetetracetic acid (EDTA)

Matheson, Coleman and Bell, Reagent, A.C.S., powder ethylenediaminetetracetic acid, disodium salt was used without further purification. It was standardized with standard copper(II) at pH 10 using murexide as an indicator (14).

Nickel(II) chloride

Solutions of nickel(II) chloride were prepared from J. T. Baker, Analyzed Reagent nickel(II) chloride hexahydrate and standardized against standard EDTA at pH 10 using murexide as an indicator (14).

Boric acid - sodium borate buffer

Solutions of a mixture of 0.1M boric acid and 0.1M sodium borate decahydrate with varying amounts of mannitol yielded buffers with a pH range from 4.0 to 9.0. Table 1 lists the amount of mannitol needed to achieve various pH values.

Ammonia-ammonium chloride buffer

A pH 10 buffer was prepared by dissolving 70 grams of ammonium chloride in 1 liter of water containing 570 ml ammonium hydroxide.

Acetic acid - Sodium acetate buffer

A pH 5 buffer was prepared by dissolving 273 grams of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in one liter of H_2O containing 60 ml of 1N HCl.

Ionic strength

A 2M sodium perchlorate solution was prepared by dissolving 245 grams of anhydrous NaClO_4 in water and making the volume up to the mark in a one-liter volumetric flask.

Anhydrous ethylenediamine

Anhydrous ethylenediamine was prepared from 250 ml ethylenediamine (98-100%) obtained from Matheson, Coleman and Bell Co. (15) This was mixed with 30 grams of

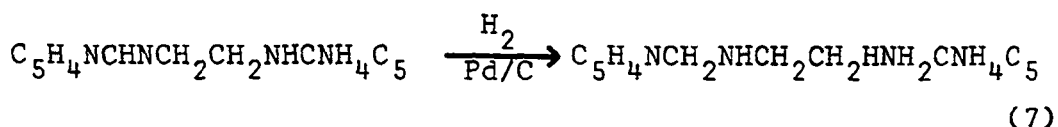
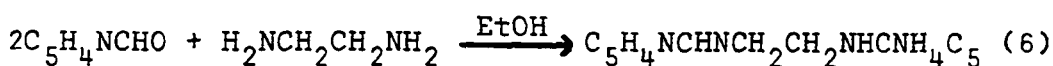
TABLE 1
pH AS A FUNCTION OF % MANNITOL BY WEIGHT
IN 0.1M H_3BO_3 and 0.1M $\text{Na}_2\text{B}_4\text{O}_7$

Mannitol (%)	pH
1.2	8.39
2.5	7.96
5.0	7.06
7.5	6.13
10.0	5.46
12.5	5.01
15.0	4.74
20.0	4.37
25.0	4.13
30.0	3.98

sodium hydroxide and the solution digested over a steam bath for about 15 hours. After digestion, the solution turned yellow and was distilled at atmospheric pressure. The fraction boiling at 116 - 116.5°C was collected and stored in a 500-ml reagent bottle in a nitrogen atmosphere.

N,N'-bis(2-picolyl)ethylenediamine

N,N'-bis(2-picolyl)ethylenediamine was prepared as shown in reactions 6 and 7 (16).



Sixty grams (.56 moles) of pyridine-2-aldehyde, Aldrich Chemical Co., were dissolved in 100 ml of absolute ethanol in a 500-ml round bottom flask. To this solution 17.0 grams (0.28 moles) of anhydrous ethylenediamine were added, whereupon a considerable amount of heat was evolved. After standing for 30 minutes the solvent was removed by warming to about 60°C under vacuum. As the last of the solvent was removed the product, bis(2-pyridinal)ethylenediimine, solidified as a tan wax-like cake. It was removed by extracting into several 150-200 ml portions of hot, low-boiling petroleum

ether (30-60°C), from which it crystallized on cooling. Recrystallization from petroleum ether gave a product melting at 66.5 - 67°C as compared to a literature value of 67 - 68°C (17).

An alcoholic solution containing 36 grams (.15 moles) of bis(2-pyridinal)ethylenediimine and 1.5 grams of 10% Pd-C catalyst (Sargent-Welch) was reduced for 4 to 5 hours in a Parr hydrogenation apparatus at 50 p.s.i. pressure and at room temperature. The catalyst was filtered off and the solvent removed under vacuum. The yellow viscous liquid, N,N'-bis(2-picolyl)ethylenediamine, which remained was distilled at 24 mm of pressure. The fraction boiling at 140 - 145°C was collected. The resulting yellow liquid was diluted with anhydrous ether and the tetrahydrochloride precipitated by passing hydrogen chloride through the solution. Recrystallization from methanol, ether (4:1) yielded colorless crystals which melted at 208.5 - 209°C as compared to a literature value of 208 - 208.5°C (16). Analysis for $C_{14}H_{22}N_4Cl_4$

	%C	%H	%N
Calculated	43.52	5.69	14.43
Found	42.63	5.51	14.28

The tetrahychloride was dissolved in deionized water and standardized against both standard Cu(II) and Ni(II) solutions using the mole-ratio method.

N,N'-dibenzylethylenediamine dihydrochloride

Thirty grams of N,N'-dibenzylethylenediamine (Aldrich Chemical Co.) were diluted with 400 ml of anhydrous ether and hydrogen chloride was bubbled through the solution. The dirty white precipitate was separated and recrystallized twice using hot absolute methanol. The material sublimated at $> 270^{\circ}\text{C}$.

Eight grams of this ligand was dissolved in about 500 ml of water and standardized potentiometrically against standard carbonate-free sodium hydroxide solution.

EXPERIMENTAL

Standardization and Determination of pK Values of DBEDA

Potentiometric titrations were used to determine the proton association constants of DBEDA and to standardize the ligand solution. Two ml of ligand stock solution (~.05M) were transferred by pipet to a flask containing 5.0 ml of 2M NaClO_4 and the volume diluted to 100 ml. This solution was then quantitatively transferred to the four-necked flask immersed in a constant temperature bath regulated to $25 \pm 0.1^\circ\text{C}$. The four-necked flask was equipped with a stirrer, glass and calomel electrodes, and nitrogen bubbler. Nitrogen was bubbled through the solution for at least 15 minutes prior to the titration. The titration was carried out by the addition of standard carbonate free sodium hydroxide solution from a 5-ml buret. The results are shown in Table 2 and represented graphically in Figure 1. The concentration of the ligand was calculated by determining the volume of sodium hydroxide used to the first neutralization point. The ionization constants were calculated by the method of Schwarzenbach (18) as described by Jonassen and Westerman (19) (see appendix).

TABLE 2

EXPERIMENTAL DATA FOR POTENTIOMETRIC TITRATION
OF DBEDA WITH NaOH

NaOH = .0854 M

 μ = .1 MT = 25 \pm .1 $^{\circ}$ C

NaOH (ml)	Moles base added- per mole of ligand,a	pH
0.00	0.00	4.510
0.11	0.183	5.110
0.21	0.349	5.385
0.30	0.498	5.560
0.40	0.664	5.724
0.50	0.830	5.874
0.60	0.996	6.018
0.69	1.146	6.140
0.80	1.330	6.320
0.90	1.495	6.486
1.00	1.661	6.690
1.14	1.890	7.085
1.22	2.026	7.480
1.29	2.140	7.808
1.42	2.358	8.230
1.59	2.641	8.570
1.70	2.824	8.730
1.80	2.990	8.868
1.90	3.156	9.000
2.00	3.322	9.124
2.11	3.505	9.250
2.22	3.687	9.410

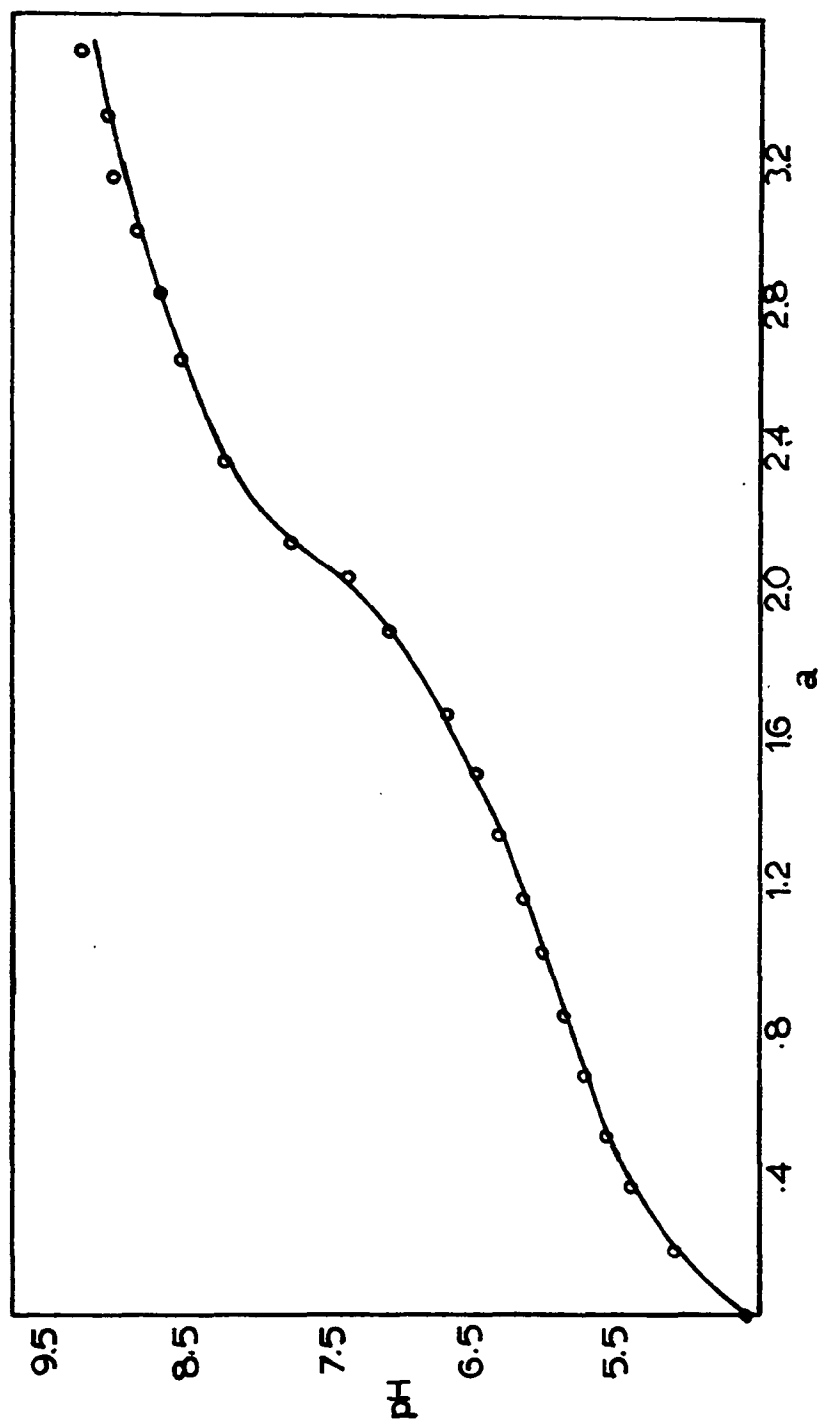


FIGURE 1. Titration of DBEDA with NaOH

a = The apparent degree of neutralization

Data was taken from the neutralization curve in the regions where ratio of moles of base to moles of ligand was approximately 0.5 and 1.5. All possible combinations of these points were used to obtain values of K_{H_2L} and K_{HL} . These values, along with those for BPEDA are listed in Table 3.

TABLE 3

PROTONATION ASSOCIATION CONSTANTS FOR DBEDA
AND BPEDA AT T = 25°C, μ = 0.1 M.

Ligand	Log K_{H_4L}	Log K_{H_3L}	Log K_{H_2L}	Log K_{HL}	Ref
DBEDA	---	---	6.02±.03	8.85±.02	This work
BPEDA	1.8	2.0	5.47	8.28	20
BPEDA	1.62	1.81	5.45	8.23	16

Spectrophotometric Study of Reactants and Products

The spectra of all reactants and products of equations 4 and 5 were obtained from 200 to 800 nm. The maximum absorbance of $\text{Cu}(\text{BPEDA})^{+2}$ and $\text{Ni}(\text{BPEDA})^{+2}$ was at 610 nm and 560 nm respectively. These wavelengths were used for the mole-ratio plot standardization of BPEDA. For kinetic studies the maximum absorbance difference between reactants and products was seen at 300 nm and 235 nm for $\text{Ni}(\text{BPEDA})^{+2}$ and $\text{Ni}(\text{BPEDA})^{+2}$ respectively.

The molar absorptivity of $\text{Ni}(\text{BPEDA})^{+2}$ was 172 at 300 nm. The molar absorptivity of BPEDA varied with pH at 300 nm. No effort was made to calculate molar absorptivities of individual species. The following data illustrate the behavior of a $2.06 \times 10^{-3}\text{M}$ solution in 10 cm cell at 300 nm: pH, A; 4.75, 0.515; 5.63, 0.327; 6.57, 0.227; 8.59, 0.437; 9.44, 0.490.

The following procedure was used to determine the molar absorptivities of DBEDA, $(\text{HDBEDA})^{+}$ and $(\text{H}_2\text{DBEDA})^{+2}$.

A 1.0 ml portion of approximately $5 \times 10^{-2}\text{M}$ DBEDA was transferred to a 50-ml beaker containing 2.5 ml of 2M NaClO_4 and 40 ml water. The pH of the solution was adjusted to the desired value by .1M NaOH. The solution was quantitatively transferred to a 50-ml flask

and diluted to volume. The pH of the solution was then measured and the absorbance of the solution recorded using the Cary spectrophotometer. This was done at pH 11 - 12 where only [L] exists, at pH 2.5 - 3.0 where only $[H_2L^{2+}]$ exists and at several intermediate pH's. Values of the molar absorptivities of $[H_2L^{2+}]$ and [L] were calculated using the low pH and high pH solutions respectively. The molar absorptivities of $[HL^+]$ was then calculated from the absorbance at intermediate pH values using the following equation:

$$A = \epsilon_L[L] + \epsilon_{HL}[HL] + \epsilon_{H_2L}[H_2L] \quad (8)$$

where A is the total absorbance.

The experimental conditions and results are shown in Table 4.

Determination of Formula, ϵ , and K_{stab} of $Ni(DBEDA)^{+2}$

The formula and ϵ of the complex were determined using a mole-ratio plot with a constant known amount of Ni(II) and varying amounts of ligand.

A stock solution of Ni(II) was diluted to $3.90 \times 10^{-5}M$ in 50-ml volumetric flasks and varying amounts of diluted ligand stock solution were then transferred to the flasks. Boric acid - sodium borate buffer were used to maintain a constant pH of 8.9. The absorbance and

TABLE 4

EXPERIMENTAL CONDITIONS AND RESULTS FOR THE DETERMINATION OF MOLAR ABSORPTIVITIES OF DBEDA, $[L]$; HDBEDA⁺, $[HL^+]$; H₂DBEDA⁺², $[H_2L^{+2}]$.

Total ligand = $1.03 \times 10^{-3} M$, μ = .1 M, Cell path length = 1.0 cm,

Wavelength = 235 nm, Light source = hydrogen lamp

pH	$[L] \times 10^3, M$	$[HL^+] \times 10^3, M$	$[H_2L^{+2}] \times 10^3, M$	Absorb.
2.36			1.03	.0862
2.51			1.03	.0861
2.94			1.03	.0870
3.00			1.03	.0880
5.70		.333	.697	.108
6.02		.515	.515	.118
6.49	.00335	.767	.259	.136
6.99	.0127	.917	.0928	.150
7.33	.0288	.954	.0467	.153
8.03	.134	.886	.00862	.169
11.23	1.03			.285
11.43	1.03			.287
11.95	1.03			.286
12.11	1.03			.288

Average ϵ_L = 278 ± 1

Average ϵ_{HL} = 149 ± 2

Average ϵ_{H_2L} = $84.2 \pm .4$

the pH of each flask were measured. The results are shown in Table 5. A plot of absorbance vs. ligand concentration was prepared and is shown in Figure 2. From the plot there appears to be an inflection in the curve at 3.96×10^{-5} M ligand concentration indicating the formation of 1:1 complex, however, at higher concentration of ligand the curve is essentially linear making it difficult to establish the presence of $\text{Ni}(\text{DBEDA})_2^{+2}$ or $\text{Ni}(\text{DBEDA})_3^{+2}$.

The absorbance of the complex at the extrapolated inflection in the plot was 0.364. The absorbance due to the excess ligand at that point was subtracted and the molar absorptivity of $\text{Ni}(\text{DBEDA})^{+2}$ calculated to be 778.

The stability constant of the complex was determined by measuring the absorbance of solutions containing a fixed amount of Ni(II) and total DBEDA. Each solution was at a different pH and provided a different DBEDA concentration. Table 6 shows the experimental conditions and absorbance data. The stability constant was then calculated from the following expressions.

$$A_{\text{total}} = A_{\text{NiL}} + A_{\text{L}} + A_{\text{HL}} \quad (9)$$

where L refers to DBEDA.

TABLE 5

ABSORBANCE AND CONCENTRATION DATA USED FOR
MOLE-RATIO PLOT OF Ni(II) AND DBEDA.

$[\text{Ni}^{+2}] = 3.90 \times 10^{-5} \text{M}$, Temp. = $25 \pm .1^\circ \text{C}$, pH = 8.9

Wavelength = 235 nm,

Cell path length = 10 cm

$[\text{L}] \times 10^5, \text{M}$	Absorbance	$[\text{L}] \times 10^5, \text{M}$	Absorbance
0.5	.100	6.0	.451
1.0	.140	7.0	.500
1.5	.182	8.0	.543
2.0	.225	9.0	.585
2.5	.250	10.0	.625
3.0	.282	11.0	.670
3.5	.310	12.0	.700
4.0	.344	15.0	.861
4.5	.362	20.0	1.04
5.0	.392	25.0	1.25
5.5	.410		

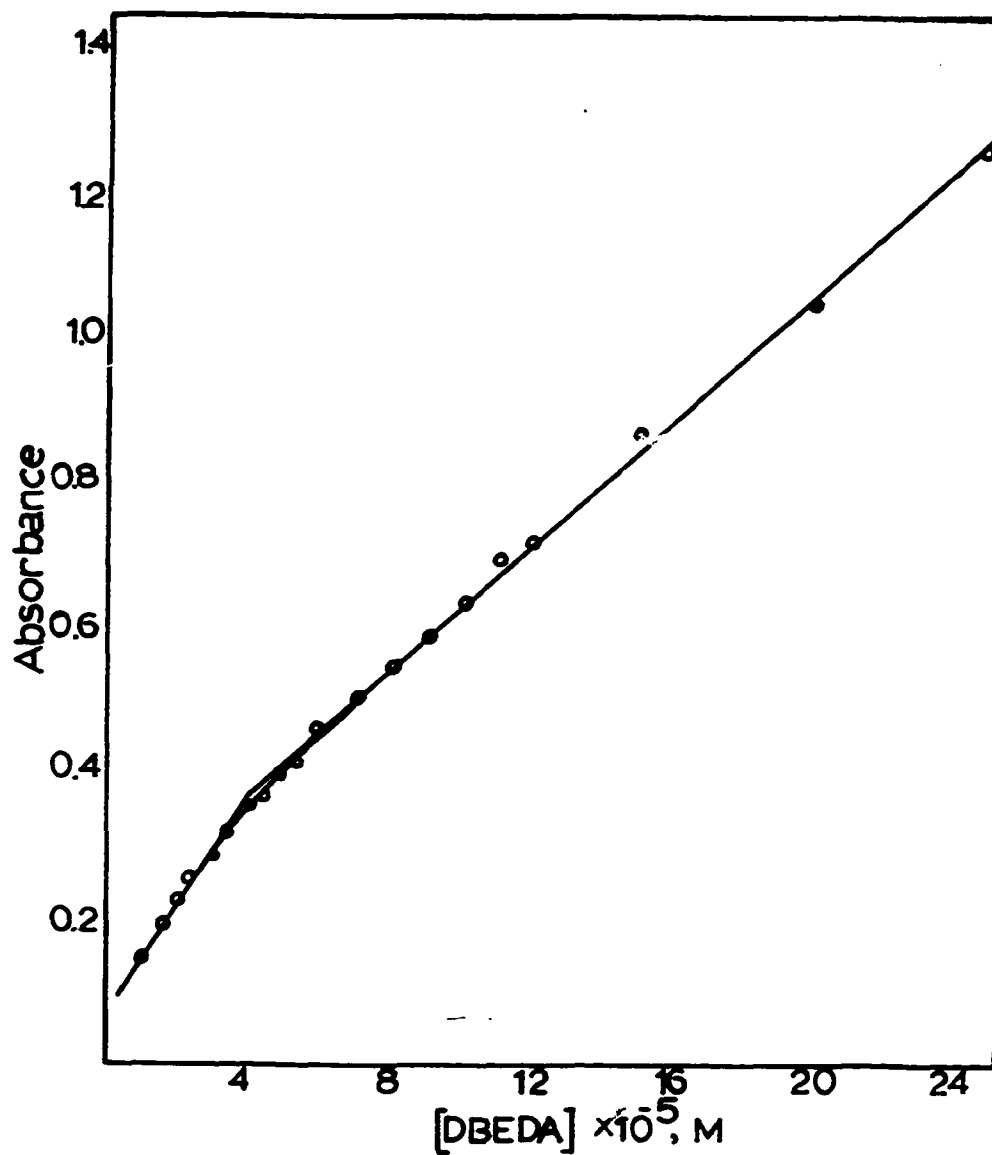


FIGURE 2. Mole-ratio plot of Ni(DBEDA)⁺²

TABLE 6

EXPERIMENTAL CONDITIONS USED FOR THE DETERMINATION OF THE STABILITY CONSTANT OF $\text{Ni}(\text{DBEDA})^{+2}$

$[\text{Ni}^{+2}] = 8.25 \times 10^{-5} \text{ M}$, $[\text{DBEDA}] = 1.65 \times 10^{-4} \text{ M}$

Cell path length = 10 cm, Wavelength = 235 nm

$\mu = 0.1\text{M}$

pH	Absorbance	$K_{\text{stab}} \times 10^{-5}$
8.65	.653	2.20
8.98	.725	1.24
9.23	.779	1.40
9.25	.776	1.22
9.36	.810	2.10
9.45	.815	1.74
9.55	.820	1.92
9.98	.841	2.30
Avg. $K_{\text{stab}} = 1.77 \pm .41 \times 10^5$		

$$A_{\text{total}} = \epsilon_{\text{NiL}}[\text{NiL}] + \epsilon_{\text{L}}[\text{L}] + \epsilon_{\text{HL}}[\text{HL}] \quad (10)$$

$$= \epsilon_{\text{NiL}}[\text{NiL}] + [\text{L}] \left(\epsilon_{\text{L}} + \frac{[\text{H}^+]}{K_2} \epsilon_{\text{HL}} \right) \quad (11)$$

Here K_2 is the second acid dissociation constant of DBEDA.

Defining β as the fraction of DBEDA relative to the total and substituting into equation 11 for $[\text{L}]$

$$A_{\text{total}} = \epsilon_{\text{NiL}}[\text{NiL}] + \left(\beta_{\text{L}}([\text{L}]_{\text{t}} - [\text{NiL}]) \right) \left(\epsilon_{\text{L}} + \frac{[\text{H}^+]}{K_2} \epsilon_{\text{HL}} \right) \quad (12)$$

On rearranging, equation 12 becomes

$$[\text{NiL}] = \frac{A_{\text{t}} - [\text{L}_{\text{t}}] \beta_{\text{L}} \epsilon_{\text{L}} - \text{L}_{\text{t}} \beta_{\text{L}} \epsilon_{\text{HL}} \frac{[\text{H}^+]}{K_2}}{\epsilon_{\text{NiL}} - \beta_{\text{L}} \epsilon_{\text{L}} - \beta_{\text{L}} \epsilon_{\text{HL}} \frac{[\text{H}^+]}{K_2}} \quad (13)$$

$$K_{\text{stab}} = \frac{[\text{NiL}]}{[\text{Ni}][\text{L}]} \quad (14)$$

Substitution of NiL into equation 13 yields

$$K_{\text{stab}} = [\text{NiL}] / \left([\text{Ni}_{\text{t}}] - [\text{NiL}] \right) \left([\text{L}_{\text{t}}] - [\text{NiL}] \right) \quad (15)$$

Kinetics of the Reaction of Ni(II) with BPEDA and DBEDA

The kinetics of the reactions of Ni(II) with BPEDA and DBEDA were studied by following the increase in absorbance due to the formation of $\text{Ni}(\text{BPEDA})^{+2}$ and $\text{Ni}(\text{DBEDA})^{+2}$ respectively, using the stopped-flow technique. These reactions were studied under pseudo-first order conditions over the pH range of 9.3 to 4.2 for BPEDA and 8.5 to 7.0 for DBEDA. The experimental conditions are summarized in Table 7. The solutions were prepared as follows.

Boric acid - sodium borate buffer solutions of different pH values were prepared by adding varying amounts of mannitol to a known volume of boric acid - borate buffer. Each (Ni(II) solution was prepared by diluting Ni(II) stock solution to the required concentration in a 25-ml volumetric flask containing above prepared buffer solution and sodium perchlorate to maintain the ionic strength. Solutions of the ligand at various pH values were prepared by diluting the appropriate volumes of ligand stock solution in 25-ml volumetric flasks containing buffer. The pH of ligand solution, if different, was brought close to the pH of Ni(II) solution by adding small amounts of NaOH, HClO_4 or mannitol. All flasks were then placed into the thermostated waterbath

TABLE 7
EXPERIMENTAL CONDITIONS USED FOR REACTION RATE STUDIES

BPEDA		DBEDA	
[Ni ⁺²]	= .984 x 10 ⁻³ M	[Ni ⁺²]	= 1.97 x 10 ⁻⁴ M
[BPEDA]	= 1.01 x 10 ⁻² M	[DBEDA]	= 2.06 x 10 ⁻³ M
Ionic strength	= 0.1 M	Ionic strength	= 0.1 M
pH range	= 9.25 - 4.20	pH range	= 8.52 - 6.95
Temperature	= 25±.1°C	Temperature	= 25±.1°C
Wavelength	= 300 nm	Wavelength	= 235 nm
Slit width	= 0.21 mm.	Slit width	= 0.15 mm.
Light source	= Hydrogen Lamp	Light source	= Hydrogen Lamp
Nitrogen pressure	= 60 p.s.i.	Nitrogen pressure	= 60 p.s.i.
Cell path length	= 1 cm	Cell path length	= 1 cm

maintained at $25 \pm 0.1^\circ \text{C}$ for at least 20 - 30 minutes. The stopped-flow spectrophotometer was set at the appropriate wavelength and slit. The oscilloscope was calibrated to full scale deflection for 0% T and 100% T. The syringes were then filled with the Ni(II) and ligand solutions and the stopped flow cell filled with product. The resulting oscilloscope trace was adjusted to the bottom of the screen using a "bucking voltage". The sensitivity and/or gain was then increased until almost full scale deflection was obtained for the reaction trace. All traces were recorded on Polaroid film. At least two to three runs were made for each set of conditions. A similar procedure was used for each pH. The pH of the reaction was measured by mixing 10.0 ml Ni(II) and 10.0 ml ligand solution adjusted to the same pH. In all cases there was no pH change upon mixing.

Kinetic measurements could not be made of pH values greater than 9.25 due to the precipitation of Ni(OH)_2 . Values lower than pH 4 were impractical because of lack of a suitable buffer.

The rate expression for reactions 4 and 5 can be expressed by the following equation.

$$-\frac{d[\text{Ni}^{+2}]}{dt} = \frac{d[\text{NiL}^{+2}]}{dt} = k [\text{Ni}^{+2}]^n [\text{L}_{\text{total}}]^m \quad (16)$$

where L is either BPEDA or DBEDA and $[\text{Ni}^{+2}]_0$ is the initial concentration. With a 10-fold excess of ligand over nickel, the concentration of ligand remains essentially constant during the reaction and integration of equation 16 with respect to time and concentration with $n=1$ gave equation 17.

$$\log[\text{Ni}^{+2}] = \log[\text{Ni}^{+2}]_0 - k_0 t / 2.303 \quad (17)$$

Here k_0 is a pseudo-first order rate constant.

$$k_0 = k[\text{L}_{\text{total}}]^m \quad (18)$$

Plots of $\log(A_\infty - A_t)$, proportional to $\log[\text{Ni}^{+2}]$, vs. time showed excellent linear behavior, establishing first-order behavior in Ni(II). An example is shown in Figure 3.

The order in ligand was established by obtaining the rate constant, k_0 , at various concentration of total ligand at the same pH. A plot of k_0 vs. $[\text{L}_{\text{total}}]$ gave a straight line for both BPEDA and DBEDA, thus establishing first-order behavior in both ligands. Tables 8 and 9 show the values of k_0 as a function of pH and ligand concentration for DBEDA and BPEDA respectively.

Resolution of Rate Constants

In the pH ranges for which rate measurements were

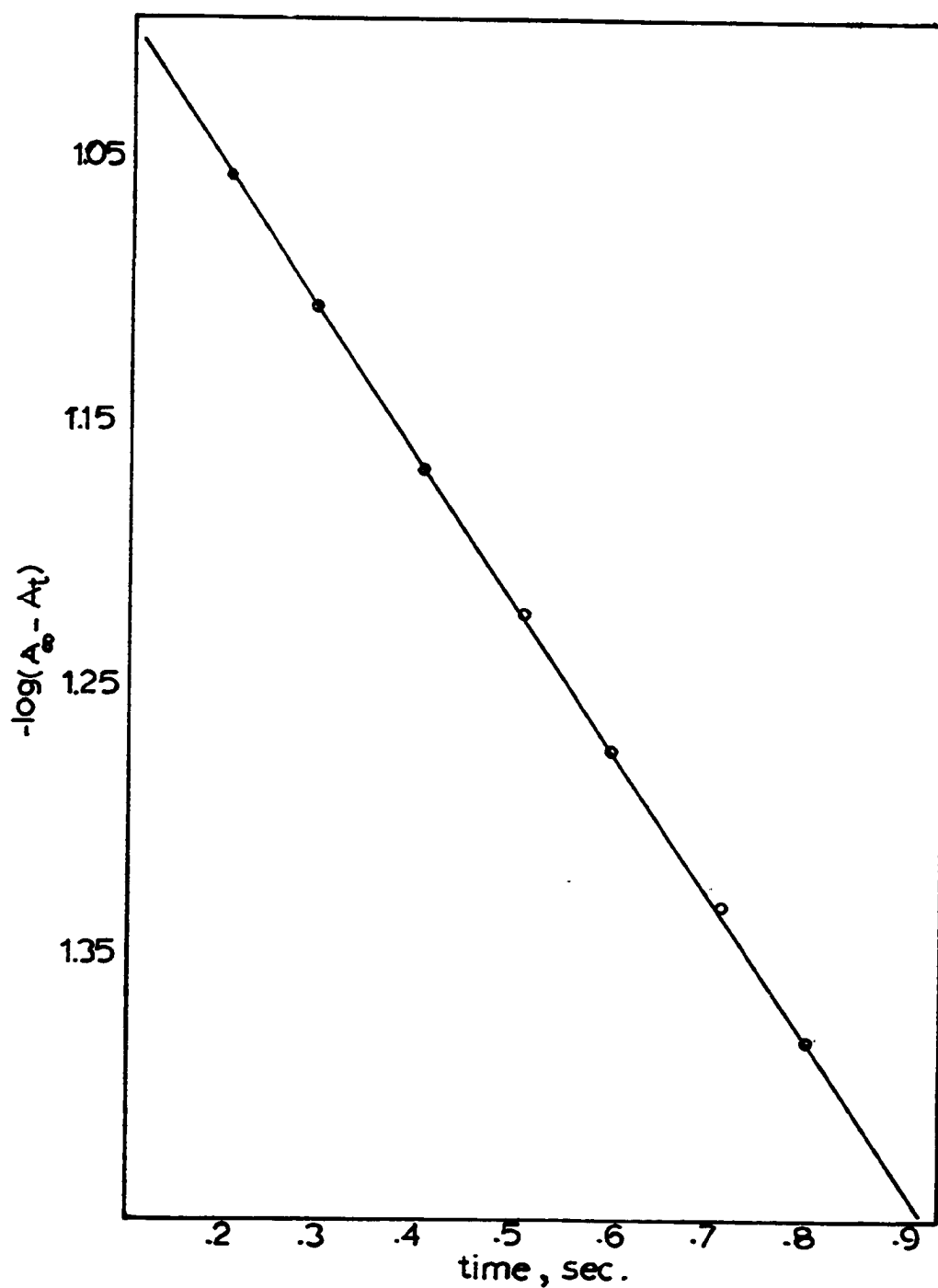


FIGURE 3. A typical first-order rate plot. Data for run No. 76.

TABLE 8

EXPERIMENTAL CONDITIONS AND RATE CONSTANTS FOR THE ORDER
OF REACTION IN LIGAND.

$[\text{Ni}^{+2}] = 9.84 \times 10^{-5} \text{M}$	$[\text{Ni}^{+2}] = 4.91 \times 10^{-4} \text{M}$
$[\text{DBEDA}] = 1.03 \times 10^{-3} \text{M}$	$[\text{BPEDA}] = 5.05 \times 10^{-3} \text{M}$
pH = 7.90	pH = 8.44
Cell path length = 1.0 cm	Cell path length = 1.0 cm
Wavelength = 235 nm	Wavelength = 300 nm
$\mu = 0.1 \text{ M}, T = 25 \pm 0.1^\circ \text{C}$	$\mu = 0.1 \text{ M}, T = 25 \pm 0.1^\circ \text{C}$

Sample No.	$[\text{DBEDA}] \times 10^3, \text{M}$	k_o, sec^{-1}
1	1.03	0.0530
2	1.03	0.0535
3	1.03	0.0537
		Avg. 0.0534 \pm .0002
4	1.55	0.0772
5	1.55	0.0766
		Avg. 0.0769 \pm .0003
6	2.06	0.101
7	2.06	0.103
8	2.06	0.108
		Avg. 0.104 \pm .002
9	2.57	0.124
10	2.57	0.127
11	2.57	0.130
		Avg. 0.127 \pm .002

TABLE 8 (cont.)

12	3.09	0.157
13	3.09	0.159
14	3.09	0.155
		Avg. $0.157 \pm .001$
15	3.61	0.187
16	3.61	0.184
17	3.61	0.181
		Avg. $0.184 \pm .002$
18	4.12	0.210
19	4.12	0.215
20	4.12	0.211
		Avg. $0.212 \pm .002$
	[BPEDA] $\times 10^3, M$	
21	5.05	6.13
22	5.05	6.08
		Avg. $6.10 \pm .02$
23	7.57	8.98
24	7.57	8.91
25	7.57	8.96
		Avg. $8.95 \pm .02$
26	10.1	11.8
27	10.1	12.2
28	10.1	12.1
		Avg. $12.0 \pm .01$
29	12.6	15.4
30	12.6	15.0
31	12.6	15.2
		Avg. $15.2 \pm .1$
32	15.2	18.0
33	15.2	18.5
34	15.2	18.4
		Avg. $18.3 \pm .2$

TABLE 9
KINETIC DATA FOR THE FORMATION
OF $\text{Ni}(\text{DBEDA})^{+2}$ and $\text{Ni}(\text{BPEDA})^{+2}$

DBEDA

Sample No.	K_o, sec^{-1}	pH
35	0.236	8.52
36	0.231	8.52
37	0.234	8.52
Avg.	$0.233 \pm .002$	
38	0.217	8.44
39	0.210	8.44
40	0.215	8.44
Avg.	$0.214 \pm .003$	
41	0.168	8.28
42	0.173	8.28
43	0.169	8.28
Avg.	$0.170 \pm .002$	
44	0.156	8.14
45	0.150	8.14
46	0.151	8.14
Avg.	$0.152 \pm .003$	
47	0.116	8.00
48	0.121	8.00
49	0.124	8.00
Avg.	$0.120 \pm .003$	
50	0.108	7.94
51	0.113	7.94
52	0.110	7.94
Avg.	$0.110 \pm .002$	

TABLE 9 (Cont.)

53	0.0870	7.74
54	0.0861	7.74
55	0.0868	7.74
Avg.	0.0868±.0004	
56	0.0710	7.62
57	0.0717	7.62
58	0.0717	7.62
Avg.	0.0712±.0004	
59	0.0545	7.20
60	0.0542	7.20
61	0.0550	7.20
Avg.	0.0546±.0003	
62	0.0481	6.95
63	0.0492	6.95
64	0.0485	6.95
Avg.	0.0486±.0004	

BPEDA

<u>Sample No.</u>	<u>k_O, sec⁻¹</u>	<u>pH</u>
65	1.21	3.60
66	1.17	3.60
Avg.	1.19±.02	
67	1.28	4.20
68	1.31	4.20
Avg.	1.30±.02	
69	1.37	4.70
70	1.35	4.70
71	1.41	4.70
Avg.	1.38±.02	
72	1.46	4.90
73	1.44	4.90
Avg.	1.45±.01	
74	1.53	5.00

TABLE 9 (cont.)

75	1.56	5.00
76	1.54	5.00
Avg.	$1.54 \pm .01$	
77	1.77	5.20
78	1.83	5.20
79	1.81	5.20
Avg.	$1.80 \pm .02$	
80	2.06	5.69
81	2.04	5.69
82	1.97	5.69
Avg.	$2.02 \pm .04$	
83	2.45	6.33
84	2.48	6.33
Avg.	$2.46 \pm .02$	
85	3.00	6.60
86	2.95	6.60
87	2.93	6.60
Avg.	$2.96 \pm .03$	
88	3.12	6.80
89	3.16	6.80
90	3.17	6.80
Avg.	$3.15 \pm .02$	
91	5.02	7.52
92	5.04	7.52
93	4.97	7.52
Avg.	$5.01 \pm .03$	
94	5.30	7.60
95	5.33	7.60
96	5.27	7.60
Avg.	$5.30 \pm .02$	

TABLE 9 (cont.)

97	7.18	7.90
98	7.07	7.90
99	7.11	7.90
Avg.	$7.12 \pm .04$	
100	9.07	8.10
101	9.01	8.10
102	8.86	8.10
Avg.	$8.98 \pm .09$	
103	10.5	8.26
104	11.1	8.26
105	10.8	8.26
Avg.	$10.8 \pm .2$	
106	12.1	8.45
107	11.9	8.45
108	12.0	8.45
Avg.	$12.0 \pm .08$	
109	12.9	8.54
110	12.2	8.54
111	13.0	8.54
Avg.	$12.7 \pm .3$	
112	15.7	9.00
113	16.1	9.00
Avg.	$15.9 \pm .2$	
114	17.4	9.25
115	16.8	9.25
116	16.5	9.25
Avg.	$16.9 \pm .4$	

taken protonated forms of BPEDA and DBEDA exist. The observed rate of formation of complex includes terms involving these protonated forms. This can be expressed as shown in equation 19 where only the first two terms on the right hand side are present for DBEDA.

$$k_o = k_{Ni}^L [L] + k_{Ni}^{HL} [HL^+] + k_{Ni}^{H_2L} [H_2L^{+2}] \quad (19)$$

For BPEDA, in the pH range of 9.3 to 7.5, the concentration of $[H_2L^{+2}]$ is negligible. This is shown in Figure 4.

Equation 19 may be rearranged to

$$\frac{k_o}{[L]} = k_{Ni}^L + k_{Ni}^{HL} \frac{[H^+]}{K_{HL}} \quad (20)$$

$$\text{where } K_{HL} = \frac{[H^+][L]}{[HL^+]} \quad (21)$$

for BPEDA. A least squares plot of equation 20, shown in Figure 5, gave $k_{Ni}^L = 1.82 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ as the intercept and $k_{Ni}^{HL} = 2.63 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ from the slope. For the pH range 6.8 to 4.2, where $[H_2L^{+2}]$ is important, see Figure 4, and k_{Ni}^L is now known, equation 19 can be rearranged to

$$\frac{k_o - k_{Ni}^L [L]}{[HL^+]} = k_{Ni}^{HL} + k_{Ni}^{H_2L} \frac{[H^+]}{K_{H_2L}} \quad (22)$$

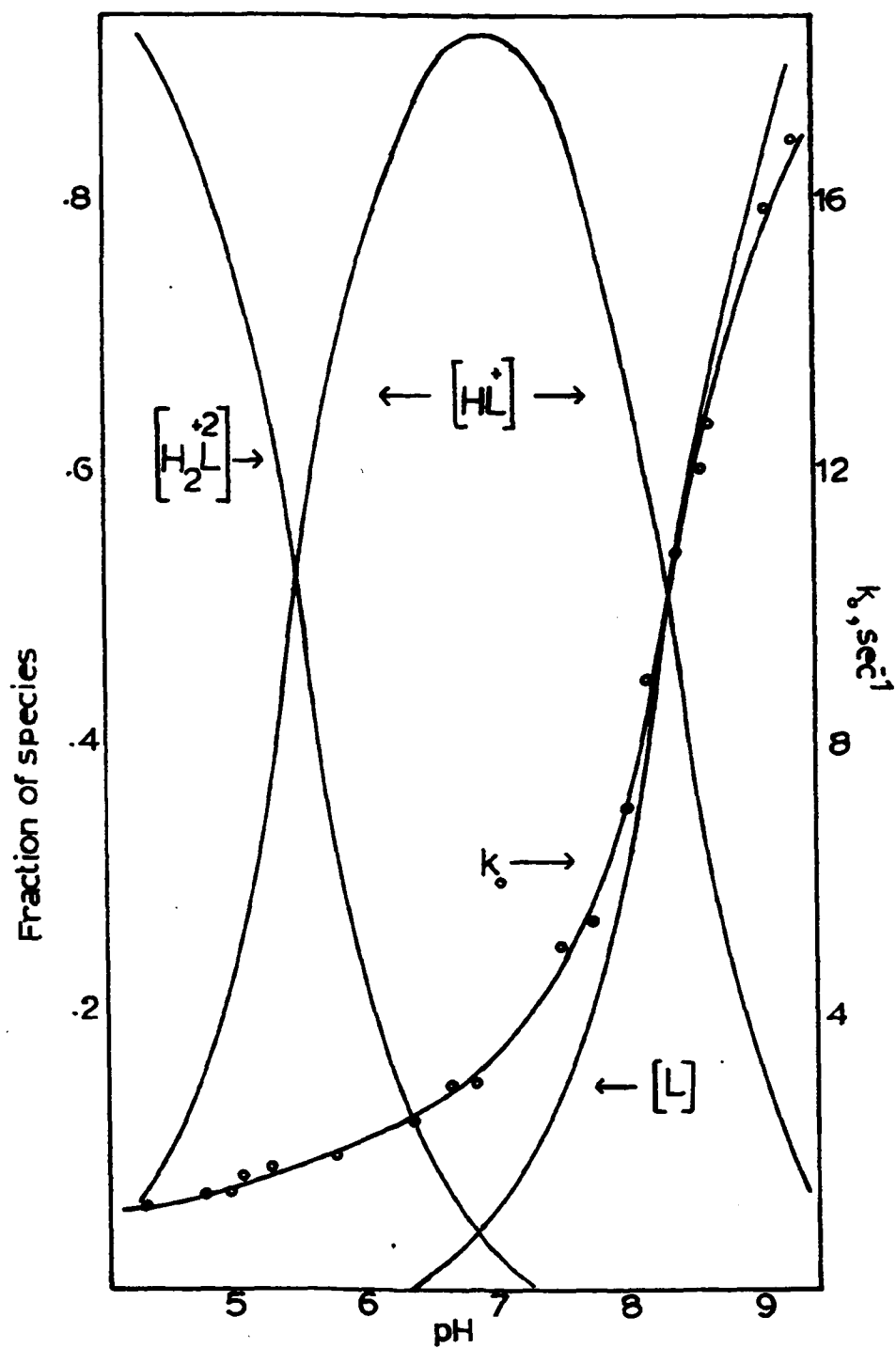


FIGURE 4. Fraction of BPEDA and k_o as a function of pH

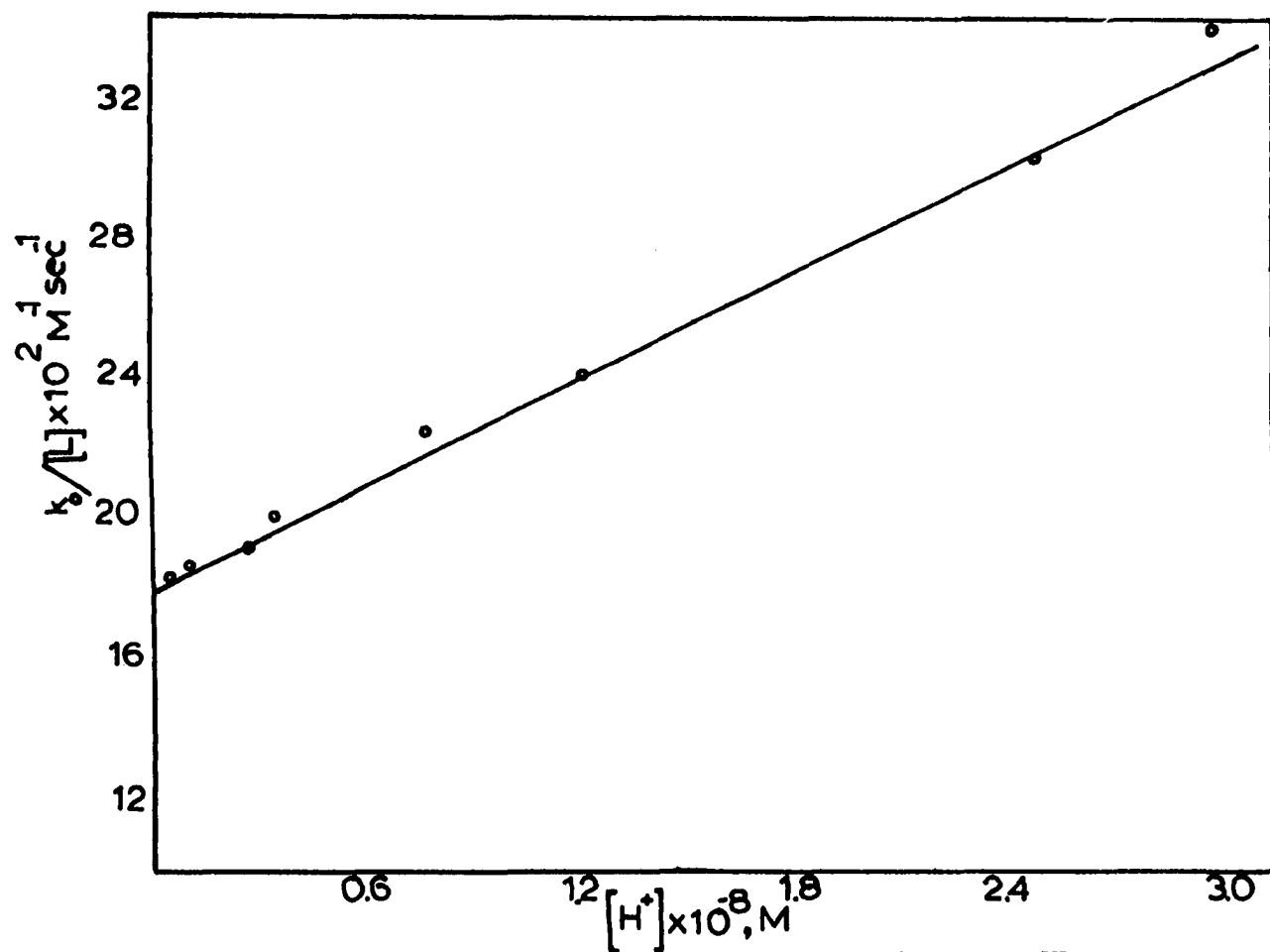


FIGURE 5. Resolution of rate constants k_{Ni}^L and k_{Ni}^{HL} for the formation of $Ni(BPEDA)^{+2}$

$$\text{where } K_{H_2L} = \frac{[H^+][HL^+]}{[H_2L^{+2}]} \quad (23)$$

for BPEDA. A least squares plot of equation 22, shown in Figure 6, gave $k_{Ni}^{HL} = 2.63 \times 10^2 M^{-1} \text{sec}^{-1}$ as the intercept and $k_{Ni}^{H_2L} = 1.15 \times 10^2 M^{-1} \text{sec}^{-1}$ from the slope.

Since only two terms would be expected for the Ni(II) reaction with DBEDA, the last term on the right-hand side of equation 19 can be dropped and the equation rearranged to the form of equation 20 where K_{HL} is the last acid dissociation constant of DBEDA. A least squares plot of equation 20 for DBEDA is shown in Figure 7 and gave $k_{Ni}^L = 3.09 \times 10^2 M^{-1} \text{sec}^{-1}$ as the intercept and $k_{Ni}^{HL} = 22.5, M^{-1} \text{sec}^{-1}$ from the slope.

For both ligands, equation 19 allows calculation of the observed rate constant as a function of pH since the resolved rate constants and appropriate ligand concentrations are known. Tables 10 and 11 list the data. Comparison of these calculated values with the experimentally observed ones gives excellent agreement for the entire pH range. This is shown in Figure 4 for BPEDA and Figure 8 for DBEDA.

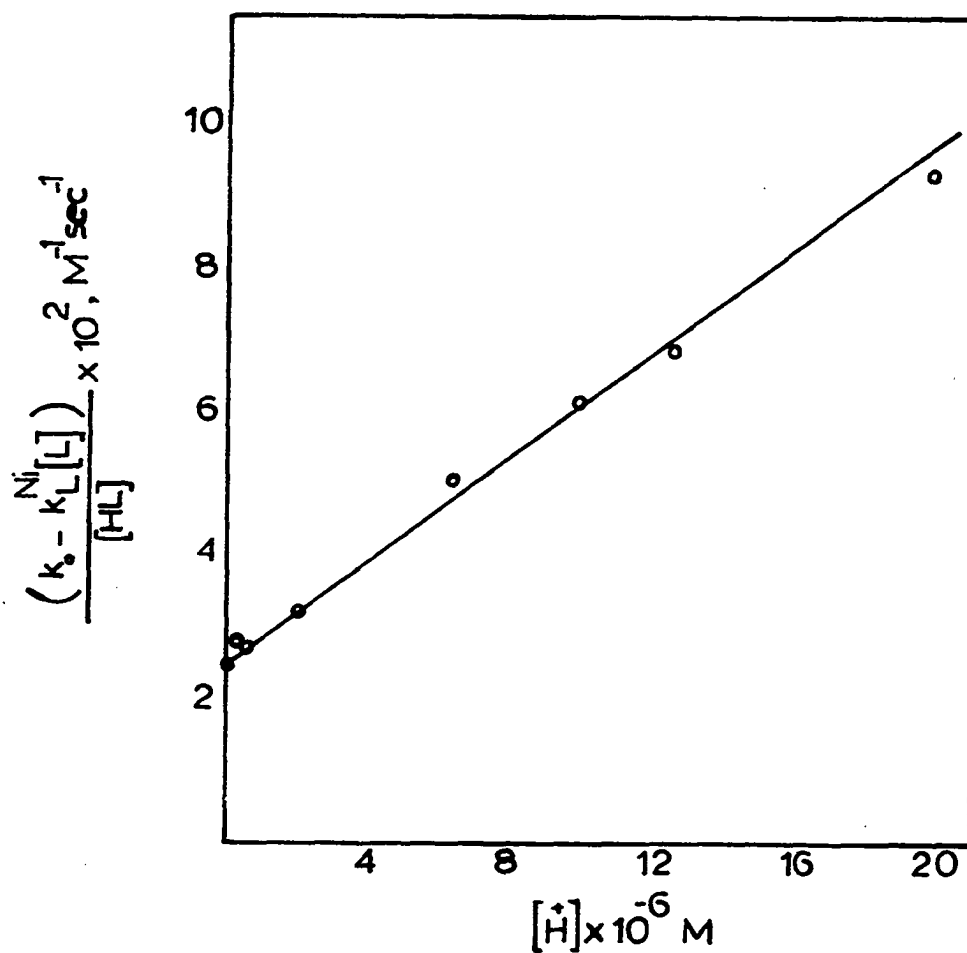


FIGURE 6. Resolution of rate constants

k_{Ni}^{HL} and $k_{Ni}^{H_2L}$ for BPEDA

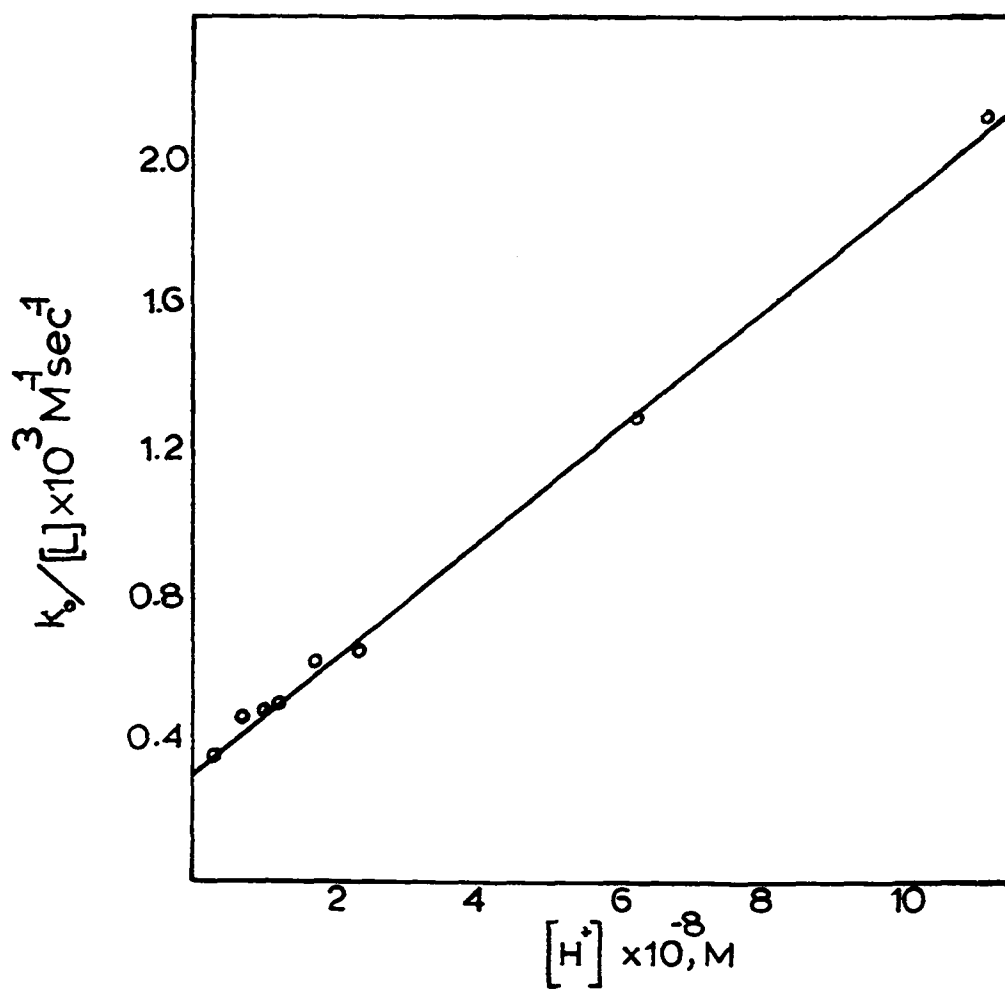


FIGURE 7. Resolution of rate constants k_{Ni}^L
and k_{Ni}^{HL} for $Ni(DBEDA)^{+2}$

TABLE 10

VALUES OF LIGAND CONCENTRATION AND pH
NECESSARY TO CALCULATE k_o for DBEDA.

$$k_{Ni}^L = 3.09 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}, \quad k_{Ni}^{HL} = 22.5 \text{ M}^{-1} \text{ sec}^{-1}$$

pH	[L] $\times 10^3$, M	[HL ⁺] $\times 10^3$, M	$k_o \text{ sec}^{-1}$ (calculated)	$k_o \text{ sec}^{-1}$ avg. (experimental)
6.95	.00229	1.82	.0481	.0486
7.20	.0423	1.89	.0559	.0546
7.62	.112	1.90	.0779	.0712
7.74	.146	1.88	.0874	.0866
7.94	.223	1.81	.110	.110
8.00	.252	1.78	.118	.120
8.14	.333	1.71	.141	.152
8.28	.434	1.61	.170	.170
8.44	.574	1.47	.210	.214
8.52	.654	1.40	.233	.233

TABLE 11

VALUES OF LIGAND CONCENTRATION AND pH NECESSARY TO CALCULATE k_o FOR BPEDA

$$k_{Ni}^L = 1.82 \times 10^3 M^{-1} sec^{-1}, k_{Ni}^{HL} = 2.62 \times 10^2 M^{-1} sec^{-1}, k_{Ni}^{H_2L} = 1.15 \times 10^2 M^{-1} sec^{-1}$$

pH	$[L] \times 10^2, M$	$[HL^+] \times 10^2, M$	$[H_2L^{+2}] \times 10^2, M$	$k_o sec^{-1}$ (calculated)	$k_o sec^{-1}$ ave. (experimental)
4.20		.0515	.962	1.22	1.30
4.70		.150	.863	1.35	1.38
4.90		.214	.795	1.45	1.45
5.00		.255	.754	1.51	1.54
5.20		.353	.656	1.61	1.80
5.69		.630	.379	2.07	2.02
6.33	.00986	.878	.119	2.61	2.46
6.60	.0193	.922	.0684	2.84	2.95
6.80	.0344	.936	.0437	3.12	3.15
7.52	.148	.863		4.95	5.01
7.60	.174	.835		5.35	5.30
7.90	.297	.713		7.27	7.12
8.10	.404	.608		8.94	8.98
8.26	4.93	.516		10.3	10.8
8.45	.603	.407		12.1	12.0
8.54	.652	.354		12.7	12.7
9.00	.850	.161		15.9	15.9
9.25	.912	.098		16.9	16.9

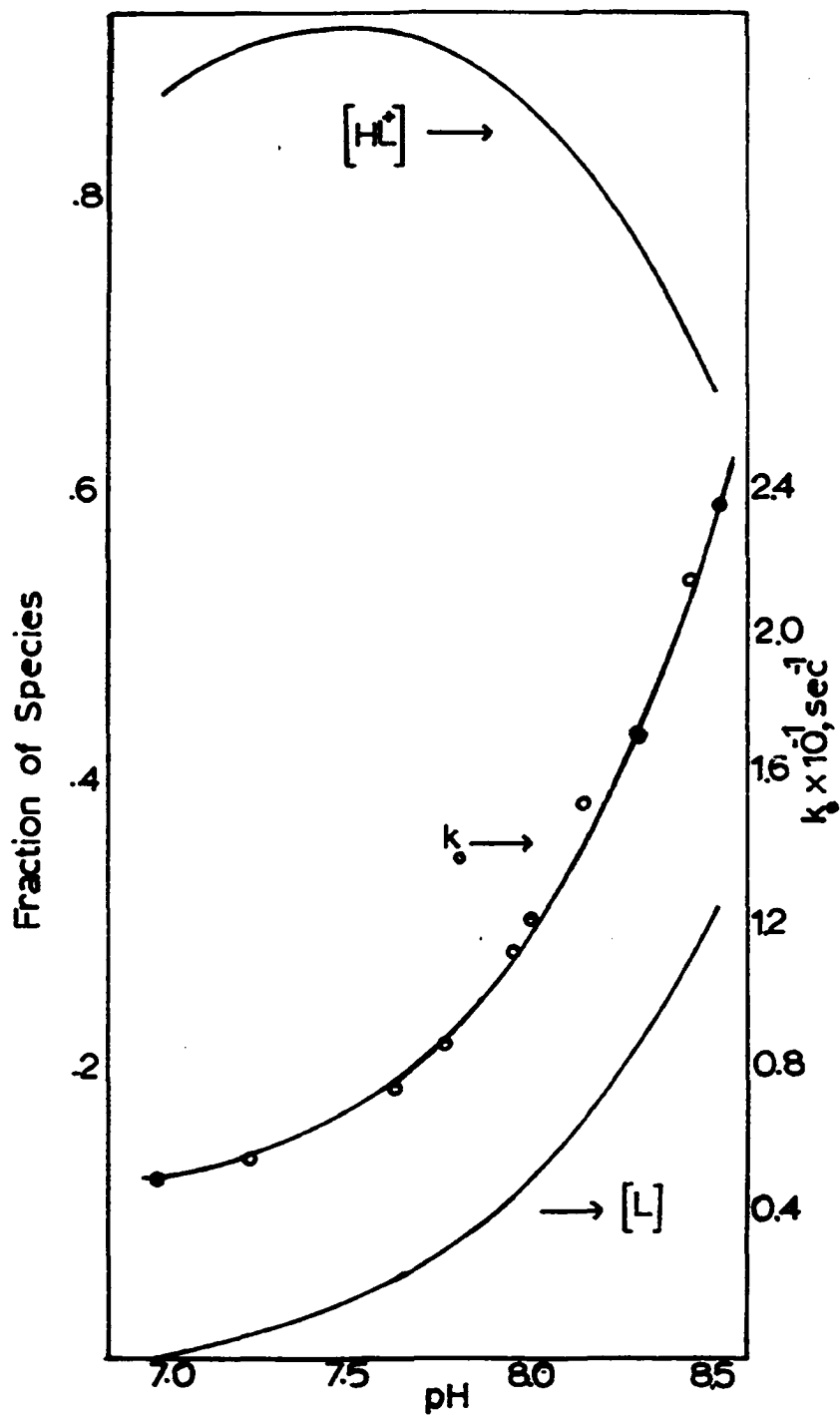


FIGURE 8. Fraction of DBEDA and k_0 as a function of pH

DISCUSSION

Specific Rate Equations

On the basis of earlier studies (2, 21, 22) nickel polyamine reactions in aqueous solution are presumed to follow a stepwise mechanism with each individual bonding step being dissociative in nature (1). On this basis the loss of a coordinated water molecule must precede the formation of each metal-donor bond and the short-lived nature of the five coordinate intermediates dictates that the reactants must be adjacent at the time of metal-water bond rupture in order for reaction to occur. Thus, the rate of initial bond formation is limited by the extent of ion-pair (outer-sphere complex) formation (1, 2).

As proposed by Wilkins (2), the reaction mechanism is represented schematically in Figure 9. Assuming that (i) outer-sphere complex formation and dissociation rates are much faster than the subsequent steps, (ii) protonated equilibria are rapidly established relative to the rate of nickel-nitrogen bond rupture, and (iii) the steady state condition may be applied for the intermediates, the rate constants in equation 19 may be related to the stepwise rate constants as

$$k_{\text{Ni}}^{\text{L}} = \frac{K_{\text{os}} k_1 k_2}{k_{-1} + k_2} \quad (24)$$

where K_{os} represents the equilibrium constant for outer-sphere complex formation and k_1 and k_2 represent the rate of water loss of the appropriate metal species. The magnitude of k_{-1} or k_2 determine whether the rate determining step is initial bond formation or ring closure.

Formation Reaction of Ni(II) with DBEDA

The reaction of Ni(II) with DBEDA is relatively simple since initial bond formation must be to an aliphatic nitrogen. The rate determining step must be either initial bond formation or ring closure. In earlier polyamine studies (21) it was concluded that, for aquonickel ion reacting with the straight-chain polyamines, $k_2 \approx 200 k_{-1}$. It was further suggested at that time, however, that the substitution of groups on the polyamine chain could slow the formation rate of successive bonds by interfering with the relation of the ligand molecule or hindering the closeness of approach to the metal ion such that later steps could become rate-determining. Since then, studies of substituted ethylenediamines have been made and it has been concluded that ring closure becomes rate-determining only for ligands more highly substituted

than N,N'-diethylethylenediamine, N,N'-diEten (11). Since DBEDA contains secondary nitrogens like N,N'-diEten and molecular models show the benzene ring is far enough removed so as to not interfere with bonding, it is safe to assume that like N,N'-diEten, initial bonding of DBEDA and not ring closure is rate-determining. Thus, $k_2 > k_{-1}$ and equation 24 becomes

$$k_{Ni}^L = K_{os} k_1 \quad (25)$$

It is possible to estimate k_{Ni}^L and k_{Ni}^{HL} from equation 25 using known values of k^{Ni-H_2O} and calculated values of K_{os} . Theoretical values of K_{os} can be calculated from equation 26 (2).

$$K_{os} = \frac{4}{3} \pi a^3 N_A 10^{-3} \exp \left[- \left[\frac{Z_1 Z_2 e_o^2}{a' D k T} - \frac{Z_1 Z_2 e_o^2 K}{D k T (1 + K a')} \right] \right] \quad (26)$$

$$\text{where } K = \left(\frac{8 \pi N_A e_o^2 \mu}{1000 D k T} \right)^{1/2}$$

N_A , Avagadro's number; μ , ionic strength; D , dielectric constant of water; k , Boltzman constant; Z_1 , charge on nickel ion; Z_2 , charge on the ligand; a center-to-center distance of closest approach between the aquonickel ion and the protonated nitrogens. Center-to-center distances have been estimated using scale molecular models. Table 12 lists the values of K_{os} calculated for various species

TABLE 12
PARAMETERS USED TO CALCULATE K_{OS} FOR VARIOUS LIGAND
SPECIES AT 25°C, $\mu = .1$ M

Ligand	$a \times 10^8, \text{cm}$	$a' \times 10^8, \text{cm}$	Z_1	Z_2	K_{OS}
DBEDA	4		+2	0	-.161
HDBEDA+	4	8	+2	+1	0.0616
BPEDA	4		+2	0	0.161
HBPEDA+	4	10	+2	+1	0.0807
H_2BPEDA^{2+}	4	9^a	+2	+2	0.0320

^aThe value of a' represents the average distance between the two protons on H_2BPEDA^{2+} and Ni(II).

of both DBEDA and BPEDA.

Substituting calculated values of K_{os} for DBEDA and HDBEDA⁺ in equation 25 with $k^{Ni-H_2O} = 2.7 \times 10^4 \text{ sec}^{-1}$ (23) and a statistical factor of two for DBEDA, yields theoretical values of $k_{Ni}^{HL} = 1.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{Ni}^L = 8.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$. The calculated values for this and other systems appear in Table 13. Calculated values for DBEDA and HDBEDA⁺ are seen to be greater than the corresponding experimental ones. Previous studies have attributed a decrease in formation rate to steric effects (10, 11, 12). In fact, even methylamine reacts slower than ammonia (10). Thus, N-benzyl-, and N-ethyl-, substituents on the aliphatic nitrogens where initial bond formation occurs certainly should have a pronounced effect on the formation rate. The relative effect of these groups can be estimated as proposed by Rorabacher (12) by calculating an organic substituent function

$$E_s = \log \frac{k}{k_o} \quad (27)$$

where k_o is a reference constant, equal to the calculated formation constant from equation 25. Values of E_s for DBEDA, HDBEDA⁺, and other related ligands are listed in Table 14. For unprotonated DBEDA, there is the possibility of rate enhancement due to an ICB effect (6) since $pK_{HL} > 8$. The difference in E_s values for DBEDA and

TABLE 13

EXPERIMENTAL AND PREDICTED FORMATION RATE CONSTANTS FOR THE REACTION OF Ni(II) WITH VARIOUS LIGANDS. PREDICTED CONSTANTS CALCULATED FROM EQUATIONS 25 and 26.

Ligand	Exp. $k_{Ni}^L, M^{-1}sec^{-1}$	Ref.	Pred. $k_{Ni}^L, M^{-1}sec^{-1}$	Ref.
DBEDA	3.09×10^2	a	8.7×10^3	a
HDVEDA ⁺	22.5	a	1.7×10^3	a
BPEDA	1.82×10^3	a	8.7×10^3	a
HBPEDA ⁺	2.63×10^2	a	4.4×10^3	a
H ₂ BPEDA ⁺²	1.15×10^2	a	1.7×10^3	a
pyridine	4×10^3	24	4.3×10^3	a
bipyridine	1.6×10^3	24	8.7×10^3	a
terpyridine ^b	1.4×10^3	24	8.7×10^3	a
1,10-phenanthroline	3.2×10^3	24	8.7×10^3	a
N,N'-diEten ^c	9.7×10^3	11	8×10^3	11
H(N,N'-diEten) ⁺	8.0	11	2×10^3	11
dimethylamine	3.32×10^2	10	4.5×10^3	10
methylamine	1.31×10^3	10	4.5×10^3	10
AMP ^d	8.6×10^3	25	4.3×10^3	a
HAMP ⁺	35	25	8.7×10^3	a
DPAe	5.8×10^3	26	8.7×10^3	a
HDPA ⁺	3.4×10^2	26	3.3×10^3	a

^aThis work; ^cN,N'-diethylethylenediamine; ^d2-aminomethylpyridine

^bPredicted value calculated assuming attack at only end nitrogens.

^edi(2-picolyl)amine

TABLE 14

STERIC FACTORS, E_s , CALCULATED FROM EQUATION 27
FOR VARIOUS LIGANDS REACTING WITH Ni(II). KIN-
ETIC DATA TAKEN FROM TABLE 9.

Ligand	E_s	Ref.
DBEDA	-1.4	a
HDBEDA ⁺	-1.9	a
BPEDA	-0.7	a
HBPEDA ⁺	-1.2	a
H ₂ BPEDA ²⁺	-1.2	a
pyridine	-0.03	a
bipyridine	-0.7	a
terpyridine	-0.8	a
1,10-phenathroline	-0.4	a
N,N'-diEten	+0.1	11
H(N,N'-diEten) ⁺	-2.3	11
methylamine	-0.5	10
dimethylamine	-1.1	10
AMP	+0.3	a
HAMP ⁺	-1.7	a
DPA	-0.2	a
HDPA ⁺	-1.0	a

^aThis work.

HDBEDA⁺ reflects this and corresponds to a modest ICB effect of about 3. This is in satisfactory agreement with the magnitude of other ICB effects relative to the corresponding ligand pK values (6, 12).

Reaction of Ni(II) with BPEDA

The reaction of Ni(II) with BPEDA involves several possibilities. The initial bond formation may be to a pyridine nitrogen and also rate-determining. The initial bond formation may be to a pyridine nitrogen but ring closure to an adjacent aliphatic nitrogen may be rate-determining. Finally, initial bond formation may be to an aliphatic nitrogen and also rate-determining. Initial bond formation to an aliphatic nitrogen with ring closure to either a second aliphatic nitrogen or a pyridine nitrogen as rate-determining can be ruled out for the same reasons that apply to DBEDA.

The pathway assuming initial, rate determining bond formation to an aliphatic nitrogen, similar to DBEDA, will be considered first. If this is correct, then similar E_s values for HDBEDA⁺ and HBPEDA⁺ should be obtained. The value of K_{OS} would be identical for both ligands and equation 27 gives $E_s = -1.2$ for HBPEDA⁺. Since no ICB effect is possible for either monoprotonated ligands, comparison of this value with that for HDBEDA⁺, $E_s = 1.9$,

shows that initial bond formation to an aliphatic nitrogen is not possible. The experimental rate for BPEDA is simply too fast. Thus, initial bond formation must be at the terminal pyridine nitrogen sites. Either this step or subsequent ring closure is rate-determining.

Location of the rate determining step may be ascertained from a consideration of Figure 9 and equation 24. The position of the rate-determining step depends upon the magnitude of k_{-1} and k_2 . The dissociation of Ni(py)^{+2} , py = pyridine, has been experimentally measured as 38 sec^{-1} (27) and may be used to approximate k_{-1} . The value of k_2 may be estimated from a study of Ni(trien)^{+2} formation (21). Initial bond formation has been shown to be rate-determining for Ni(trien)^{+2} . An estimate of k_2 has been made for trien which involves rotation of a carbon-carbon or a carbon-nitrogen bond in order to rotate a second nitrogen into a bonding position. This is followed by Ni(II) water loss. The ligands BPEDA and trien differ little in terms of rotation of a second nitrogen into a bonding position. Thus, $k_2 \approx 200 \text{ sec}^{-1}$ (21). Further evidence on the magnitude of k_2 may be obtained from the estimate $k_2 = 900 \text{ sec}^{-1}$ for N,N,N',N'-tetramethylethylenediamine which is even more highly substituted than BPEDA and trien. Thus, equation 24 also reduces to equation 25 for BPEDA with initial bond formation as rate-

determining.

The presence of an ICB effect for BPEDA may be found by calculating E_s for BPEDA and subsequent comparison to E_s for HBPEDA^+ . Since initial bond formation is to a pyridine nitrogen in both cases, steric factors will be identical. Using appropriate K_{OS} values from Table 12 in equation 25 with $k^{\text{Ni-H}_2\text{O}} = 2.7 \times 10^4 \text{ sec}^{-1}$ and a statistical factor of 2 yields $k_{\text{Ni}}^{\text{L}} = 8.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{\text{Ni}}^{\text{HL}} = 4.4 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$. Values of E_s may be calculated from equation 27 and are listed in Table 14. As with DBEDA, the difference between the two values shows a slight ICB effect of about 3. Again, in view of $\text{p}K_{\text{HL}} = 8.3$ this value is reasonable.

The reaction of Ni(II) with $\text{H}_2\text{BPEDA}^{+2}$ must also involve initial bond formation to a pyridine nitrogen since both protons occupy aliphatic nitrogen sites. Further, initial bonding must be rate-determining since the only other free nitrogen is 9 atoms removed and would result in the formation of a highly unstable 11 member ring. Using appropriate K_{OS} values from Table 12 with $k^{\text{Ni-H}_2\text{O}} = 2.7 \times 10^4 \text{ sec}^{-1}$ in equation 25 gives $k_{\text{Ni}}^{\text{H}_2\text{L}} = 1.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$. The value of E_s for $\text{H}_2\text{BPEDA}^{+2}$ and HBPEDA^+ should be equal since both involve pyridine nitrogens and neither can have an ICB effect. Equation 27 gives E_s for $\text{H}_2\text{BPEDA}^{+2}$ as -1.2 which is in excellent agreement with E_s

= -1.2 for HBPEDA^+ and lends further support for initial bonding to the pyridine nitrogens.

Comparison of Steric Effects to Other Systems

It is of interest to compare E_s values obtained from BPEDA and DBEDA with those found for other N-substituted ethylenediamines. These are listed in Table 14. Comparing monoprotonated species, N,N'-diEten shows a value similar to DBEDA. This is not unexpected since the aromatic ring of DBEDA is one carbon removed from the nitrogen donor and is planar. The larger value of E_s for monoprotonated HBPEDA^+ should be less than that of HDBEDA^+ since the substituents on the pyridine ring are constrained in the aromatic ring. The two E_s values illustrate this.

An interesting trend is seen in comparing E_s values for pyridine, bipyridine, terpyridine, 1,10-phenanthroline, HBPEDA^+ and dimethylamine. As expected, the smallest steric effect is seen for pyridine however, it is far smaller than would be expected from comparison to dimethylamine. E_s decreases significantly for bipyridine, terpyridine, assuming attack only at the two terminal nitrogens of terpyridine, show similar values and HBPEDA^+ a slightly larger value, due presumably to the rest of the molecule as a substituent in the two position of the

pyridine ring. Phenanthroline shows a rather low value in view of the fact that the second ring cannot rotate out of the way during initial bonding as is the case with the others. This may suggest some type of accelerating effect due to the close proximity of the second nitrogen during initial bonding.

Comparison of Formation Rates of Ni(II) with BPEDA, TKED, EDDA, and Trien

The ligands BPEDA, TKED, ethylenediaminediacetic acid (EDDA), and trien can all be considered as N-substituted ethylenidiamines. The position of the rate-determining step, either initial bond formation or ring closure, depends on the values of k_{-1} and k_2 in equation 24. With the exception of trien, all k_2 values should be about the same since only coordinated nitrogens appear to have a sizable effect on nickel water loss (7) and since rotational barriers would be similar. Thus, the magnitude of the dissociation constant for the N-substituted dentate group really determines the position of the rate-determining step. The strong nickel-nitrogen bonds, k^{NiPy} and k^{NiNH_3} compared to weak nickel-oxygen bonds, k^{NiOAc} and k^{NiOR} coupled with the relative inaccessibility of secondary and tertiary nitrogens cause a shift in the rate-determining step from first to second bond formation as k_{-1} increases. BPEDA having $k_{-1} = 38$

sec^{-1} fits the mechanism well.

Comparison of BPEDA with AMP and DPA

The formation reactions of Ni(II) with both free and protonated forms of 2-aminomethyl pyridine, AMP, (25) and di(2-picolyl)-amine, DPA, (26) have been measured. Again, assuming no ICB effect to be present in the protonated cases, E_s values can be calculated and are listed in Table 14. Since the monoprotonated form of both ligands involve aliphatic nitrogen protonation, the E_s values reflect steric factors for attack at the aromatic nitrogens. The value for HDPA^+ is similar to that for HBPEDA^+ as would be expected but that for HAMP^+ is abnormally low.

Calculation of E_s for AMP and DPA result in anomalously large values. In the case of DPA, pK_{HL} is < 8 (26) and no ICB effect should be present. Thus, E_s approximates the steric factor for either initial attack at an aromatic nitrogen or an aliphatic one, and can be compared to E_s for HBPEDA^+ and HDPA^+ approximating an aromatic nitrogen, or E_s for HDBEDA^+ and N,N'-diEten, approximating a secondary aliphatic nitrogen. Although E_s for DPA is higher than E_s for all the above mentioned ligands, it clearly is closer to HBPEDA^+ and HDPA^+ than HDBEDA^+ and N,N'-diEten. On this basis it is likely that, as

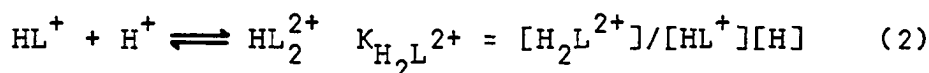
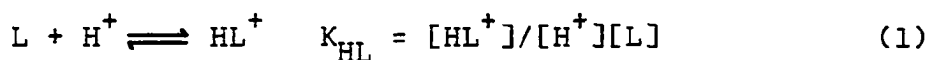
with the Ni(II) attack on BPEDA, initial attack on DPA is also through an aromatic nitrogen.

The situation involving AMP is more complex. E_s could reflect initial attack at an aromatic nitrogen but would also include an ICB effort since pK_{HL} is 8.6 (16). This would generate an ICB effect of 10 which is not unreasonable. Conversely, E_s for AMP could reflect initial attack at the aliphatic nitrogen in which case it could not be compared to E_s for $HAMP^+$ because different dentate sites would be involved although no ICB effect would be present. However, ethylamine should have a similar steric factor and comparison of E_s for $EtNH_2$ and AMP shows them to be only a factor of two apart. Thus, both mechanisms are supported by the data and a clear picture of the mechanism of Ni(II) formation with AMP cannot be established yet.

APPENDIX

APPENDIX

Basicity constants for DBEDA using the general method derived by Schwarzenbach (18). The basicity constants for DBEDA may be calculated from the neutralization curve of DBEDA · 2HCl with NaOH. The following equilibria and equations apply. DBEDA is abbreviated L in the following equations.



Total concentration of L present in solution =

$$[L_t] = [L] + [HL^+] + [HL_2^{2+}] \quad (3)$$

If a = apparent degree of neutralization of cation acid, $[HL_2^{2+}] = (\text{ml base added}) (N. \text{ base}) / (\text{conc. DBEDA}) (\text{ml soln.})$ and g = number of protons which appear on the average bound to DBEDA = true degree of neutralization, then

$$[H_t^+] = [L_t] (2-a) = [H^+] = [OH^-] + [HL^+] + 2[HL_2^{2+}] \quad (4)$$

and

$$[L_t] \times g = [HL^+] + 2[H_2L^{2+}] \quad (5)$$

but

$$g = m - a + [OH^-] - [H^+]/[L_t] \quad (6)$$

where m = maximum number of protons which may be associated with DBEDA = 2.

Combining equations 1 through 6, the following equation is obtained.

$$g + (g-1)[H^+]K_{HL} + (g-2)[H^+]^2\bar{K}_{H_2L} = 0 \quad (7)$$

where $\bar{K}_{H_2L} = K_{HL} \cdot K_{H_2L}$.

Knowing $[H^+]$, g , $(g-1)$ and $(g-2)$ can be calculated and equation 7 can be solved simultaneously for K_{HL} and K_{H_2L} .

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