8-1975

A Spectrophotometric Equilibrium Study of Nickel(II)-3, 4', 4", 4'''-Tetrasulfophthalocyanine

Stephen Lowery
Western Kentucky University

Lowery,

Stephen Nelson

1975

A SPECTROPHOTOMETRIC EQUILIBRIUM STUDY

OF

NICKEL(II)-4, 4', 4", 4'"-TETRASULFOPHTHALOCYANINE

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Stephen Nelson Lowery

August 1975

A SPECTROPHOTOMETRIC EQUILIBRIUM STUDY

OF

NICKEL(II)-4, 4', 4", 4'''-TETRASULFOPHTHALOCYANINE

Recommended _7/18/75_

Robert D. Farina
Director of Thesis

John T Riley

Norman Holy

Approved _July 22, 1975_

Elmer Gray
Dean of the Graduate School

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

toward the dimeric species. This is attributed to the increase in ion pairing brought on by the increase in ionic strength upon the addition of salt. Higher temperatures cause shifts favoring the monomeric species. The thermodynamic parameters determined for Ni^{II}-TSPC in N-methylformamide were $\Delta G^o = -4.79$ kcal/mole, $\Delta H^o = -6.22$ kcal/mole and $\Delta S^o = -4.74$ e.u.

STATEMENT OF THE PROBLEM

There have been several studies made on the effects of various central metal ions on the aggregation of tetrasulfonated phthalocyanine dye complexes in aqueous solution, but there have been no studies made on the aggregation of the nickel(II)-4, 4', 4", 4'"-tetrasulfophthalocyanine (Ni^{II}-TSPC) complex. Therefore, a study of the effects of nickel(II) on the aggregation of its aqueous tetrasulfonated phthalocyanine dye complex was proposed so that a comparison might be made with previous studies of central metal ion effects. It was found, however, that Ni^{II}-TSPC gives a much higher degree of aggregation in water than the metal complexes previously studied and that common equilibria were absent in the concentration range of 1.0×10^{-3} to 1.0×10^{-7} M. The spectra indicated the presence of a single species in this concentration range. Therefore, a comparison of the effects of nickel (II) on the aggregation of tetrasulfophthalocyanines in aqueous solutions could not be made with analogous dye systems examined previously using other transition metals.

A study of the literature revealed that there have been no studies made on the effects of a pure organic solvent on the aggregation of transition metal complexes of tetrasulfophthalocyanine dyes. Therefore, this study was made to determine such solvent effects on the Ni^{II}-TSPC complex.

1

INTRODUCTION

There have been several studies made on the aggregation
of the tetrasulfophthalocyanine transition metal complexes
in aqueous solution,[1-8] and it is well known that many solu-
tions of the tetrasulfophthalocyanine dyes in aqueous solvent
at room temperature show deviations from Beer's law over an
extended concentration range due to the presence of an equi-
librium between the dye monomer and (or) the higher dye ag-
gregate forms present. When observing the absorption spectra
of a dilute solution of these dyes in aqueous solvent, the
band of highest intensity becomes weaker as the concentration
is increased, and new bands form at other wavelengths.[9]
These changes in the spectra have been attributed to aggrega-
tion of the dye molecules to form dimers and higher polymers
under the strong dispersive forces of the chromophoric chain.[10]
In studies involving water as a solvent, the dye-dye inter-
action is in all probability not the major force causing the
molecules to associate; instead the strong solvent-solvent
interactions exclude the dye molecules from the solution and
cause them to aggregate.[11,12] In solvent systems of low
dielectric constant, the dye-dye interaction is the driving
force for the dimerization since the screening of the dye-dye
interaction is minimized in nonpolar solvents.[13]

2

equilibrium in favor of the dimer, presumably due to the increase in the ionic strength of the solution.[5]

For each monomer-dimer system, the optical absorptivities and its dimerization constant were determined either by spectrophotometric or kinetic methods. An example of the latter is the concentration-jump relaxation technique.[15] At conditions of natural or low ionic strength, the order of decreasing stability of the dimers was found to be Cu^{II}-TSPC > H_2TSPC > Fe^{III}-TSPC ≥ $(VO)^{II}$-TSPC ~ Zn^{II}-TSPC > Co^{II}-TSPC, where log K_d was found to be 8.14, 7.79, 7.11, 6.70, 6.0 and 5.47, respectively, at $25^{o}C$ except for Zn^{II}-TSPC which was obtained at $58^{o}C$.[8] The stability as measured by the equilibrium constant for dye association varies by over two orders of magnitude within the series. The lower stability of Co and Zn phthalocyanines was tentatively explained on the basis of axially coordinated water molecules inhibiting dye association. However, it has been found that both Fe^{III}-TSPC and $(VO)^{II}$-TSPC, which have coordination numbers greater than four, are more stable than the Zn and Co analogs.[16] Therefore, it can be concluded that other factors which have not been previously taken into account are operative in controlling phthalocyanine dye aggregation processes. It has been suggested by Siegel et al[8] that there are donor and acceptor qualities of metal ions which could influence the π-system of TSPC and, therefore the stability of the dimers. The major difficulty in measuring dye association processes in water is that the strong solvent-solvent interaction is the dominant

force causing the molecules to associate rather than the dye-dye interaction.

Although there have been a number of reviews on the chemistry of phthalocyanines,[17] and the absorption spectra in organic solvents have been reported in the literature for both substituted and unsubstituted phthalocyanine dyes,[18-22] there have been few studies made in organic solvents on the aggregation of the substituted or unsubstituted phthalocyanine dye complexes. Monahan et al.[23] carried out a study on the dimerization of copper(II)-4, 4', 4", 4'"-tetraoctadecyl-sulfoamidophthalocyanine (Cu^{II}-TAPC) in carbon tetrachloride and benzene, and found the dimerization constants to be 2.97 ($\pm$0.02) X 10^6 and 1.58($\pm$0.09) X 10^4 M^{-1}, respectively, at 22 $\pm$ 2°C. Using this type of phthalocyanine molecule, the dimerization process could be studied in solvents of low dielectric constant. Thus, the dye-dye interaction is the driving force for the dimerization in these solvent systems.[13] The order of decreasing dimerization for the phthalocyanine dye in several solvent systems was found to be CCl_4 > benzene > toluene > chloroform > dioxane > DHF > THF. It was found that the aggregation tendency of the dye was diminished in the solvents yielding the greatest solubility and, in general, the largest dielectric constant.

A study of the association of Cu^{II}-, Zn^{II}-, and $(VO)^{II}$-TAPC in benzene was also carried out by Monahan and his co-workers.[16] The three phthalocyanine dyes were found to exhibit a monomer-dimer equilibrium in the 1.0 X 10^{-6} to 1.0 X 10^{-4}

M concentration range, and the dimerization constants in benzene were found to be $1.58(\pm0.09) \times 10^4$, $1.09(\pm0.23) \times 10^6$, and $2.01(\pm0.49) \times 10^6$ M^{-1}, respectively.

Jones and Twigg[24] performed a study on the dissociation of the iron(II)-phthalocyanine, $(Fe^{II}-Pc)_2$, dimer in DMSO and found that when a 5.0×10^{-4} M solution of ferrous phthalocyanine was diluted one hundred fold, the peak positions were initially the same as those of the concentrated solution. However, the spectrum changed slowly to that of a dilute solution directly made up to 5.0×10^{-6} M, with clean isosbestic points. The rate of change gave reproducible first-order kinetics, with $k = 1.0 \times 10^3$ sec^{-1} at 28^oC. This rate of dissociation is of the same order of magnitude as that observed for the tetrasodium salt of cobalt(II)-4, 4', 4", 4'"-tetrasulfophthalocyanine in water,[4] and is 1.0×10^5 times slower than a water-soluble metal-free porphyrin in water.[25]

A study of the visible absorption spectra of a reactive dye based on a copper phthalocyanine chromophore (dye-SSO_3^-) as a function of concentration, temperature, pH, ionic strength, and solvent was carried out by Gruen.[26] The persistence of isosbestic points indicates the presence of an equilibrium between monomer and dimer in a concentration range of 20-0.02 mg/100 ml. The visible spectrum in water showed only relatively small changes over this concentration interval indicating a high association constant, such that the dye was almost entirely associated in this range of

concentrations. It was found that higher temperatures favored the monomeric species. Part of this disaggregation effect at higher temperatures was attributed to the reduction in the dielectric constant of water.[4] Solutions of the dye varying in pH from 4.4 to 9.2 showed no change in the absorption spectrum, which was not surprising since the reactive thiosulphate group would not be protonated until pH values of less than 2.0 are reached, and therefore, the charge on the dye remains unaltered. In various solvents, the amount of monomer present was found to increase with decreasing dielectric constant. The addition of urea was found to exert a relatively small disaggregation influence on the equilibrium.

Ahrens and Kuhn[2] carried out equilibrium studies on the sodium salt of Cu^{II}-TSPC in mixtures of ethanol and water. A 30% ethanol-water mixture of the dye was found to exhibit a monomer-dimer equilibrium in the concentration range of 3.6×10^{-7} to 3.6×10^{-5} M with concentrations greater than 3.6×10^{-5} M giving greater association of the dye. The association constant for the monomer-dimer equilibrium in a 30% ethanol-water mixture is 1.95×10^{4} l mole^{-1}. The addition of NaCl in the concentration range of 1.0×10^{-3} to 0.5 M increased the aggregation of the dye, and a new equilibrium was established between the dimer, tetramer and higher dye aggregates.

In all studies of the aggregation of tetrasulfophthalocyanine complexes in mixtures of organic solvent and water,[1,2,6,7] the presence of an organic solvent caused the

equilibrium to shift toward a lower polymeric species. Up to this time, there have been no studies of the effect of a pure organic solvent on the aggregation of tetrasulfophthalocyanine dyes reported in the literature. Therefore, this study was made on the aggregation of Ni^{II}-TSPC in N-methylformamide.

EXPERIMENTAL

This section of the thesis is composed of four parts
i.e. material, apparatus, equilibrium measurements, and pre-
liminary experiments.

A. Material

1. Tetrasodium Salt of Nickel(II)-4, 4', 4", 4'"-tetra-
sulfophthalocyanine.

The tetrasodium salt of Ni^{II}-TSPC was prepared by Charles
J. Hunt, using the methods described by Weber and Busch in
the preparation of the analogous cobalt(II) complex.[27] The
salt, a dark blue product, was kept in a vacuum dessicator to
avoid the absorption of water from the atmosphere. The puri-
ty of the complex was determined by spectral methods, and it
compared well with literature values in dimethylformamide.[18]
In N-methylformamide, maxima were found at 668, 644(shoulder),
604, and 348 nm. The molar absorptivities were 1.78 X 10^5,
3.03 X 10^4, and 2.20 X $10^4 M^{-1} cm^{-1}$ respectively.

2. N-Methylformamide

N-methylformamide of spectral quality was purchased from
the Aldrich Chemical Company, Inc. The solvent was used with-
out any further purification.

3. Sodium Perchlorate (anhydrous reagent)

The anhydrous salt of sodium perchlorate, research grade,

was purchased from the G. Frederick Smith Chemical Company, for use in adjusting the ionic strength of solutions. The salt obtained was 99% pure and was not further purified.

B. Apparatus

1. Spectral Measurement Assembly

The Cary Model 14 recording spectrophotometer was used to obtain all spectral measurements. A thermostatable sample jacket, Cary No. 1444100 was inserted in the sample compartment of the Cary Model 14 spectrophotometer to maintain the solutions at a constant temperature inside the spectral cell. A Haake Model FE constant temperature circulator pumped water through the sample jacket via 1/4 inch tygon tubing. The thermostatable cell jacket permits the solutions in the spectral cell to be maintained within $\pm$ 0.03°C at temperatures from -30°C to 55°C. A bucket of ice water served as the cold water source to the Haake circulator to prevent excessive heating during its operation. The cold water was fed to the Haake circulator via a Vertical Centrifugal Immersion Pump manufactured by Sargent-Welch Scientific Co., Model No. B-6, which was located in the bucket of ice water. Connections to and from the pump consisted of 1/4 inch tygon tubing. For extended periods of operation at low temperatures, a Forma Temp Jr bath and circulator, Model No. 2132, manufactured by the Forma Scientific Company, was used with ethylene glycol as the circulating coolant.

Cylindrical quartz cuvette cells of 0.01, 0.1, 1.0 and 10.0 cm path lengths were used for the spectrophotometric

measurements. The slidewire used in these measurements had a
0 - 2 absorption range.

2. PDP-8/I Computer

The PDP-8/I Computer manufactured by the Digital Equipment Corporation was used to expedite the equilibrium calculations. The programs used were written in "BASIC" (Beginners All-Purpose Symbolic Instruction Code) language, and are contained in the appendix at the end of this thesis.

3. Laboratory Thermometer

The Laboratory Thermometer, Model No. Bat-4, manufactured by Bailey Instruments Company, Inc. was used to accurately measure the temperature of the dye solutions while thermostating the sample spectral cell compartment. The Laboratory Thermometer has a sensor which consists of thermocouple wire of approximately .1 cm in diameter. This allows the sensor to be placed in the upper portion of the spectral cell where it will not interfere with spectral measurements; the compartment cover can then be replaced and after sufficient time has elapsed for the temperature of the solution to equilibrate, the temperature of the solution can then be measured accurately.

4. Balance

A Mettler Analytical balance, Model No. H20T, which weighs 160 gram samples with an accuracy of $\pm$ 0.01 mg was used in obtaining the weights of all compounds. The balance is a product of Fisher Scientific Company.

C. Equilibrium Measurements

A 1×10^{-2} M stock solution of Ni^{II}-TSPC (see Figure 1)

Figure 1.   Structure of Nickel(II)-4, 4', 4", 4'"-tetrasulfo-
phthalocyanine
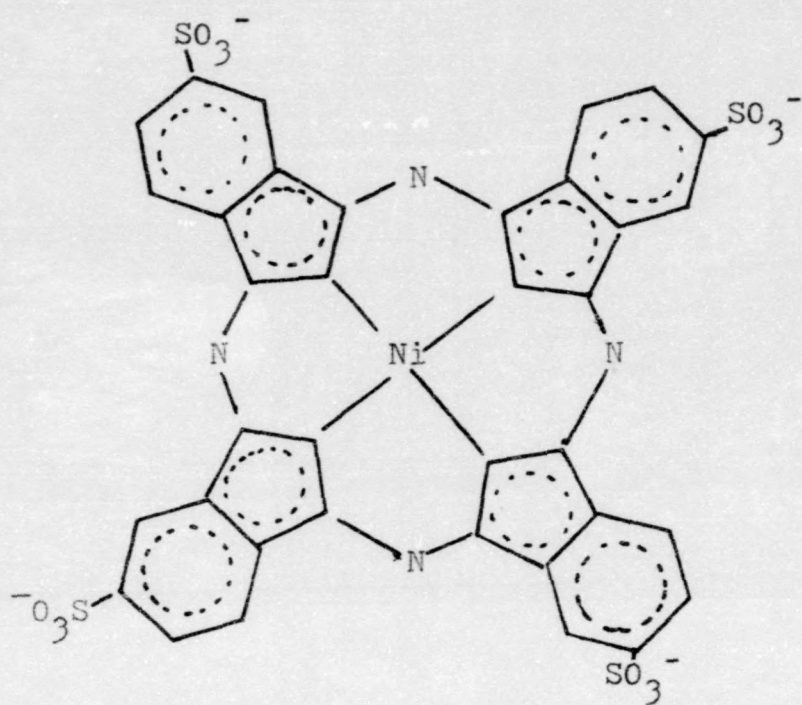
was prepared by weighing 98.00 ± 0.01 mg of the dye complex and dissolving it in 10 ml of N-methylformamide. A series of solutions ranging in dye concentration from 1.0×10^{-2} to 1.0×10^{-7} M was obtained by diluting the stock solution. Solutions were prepared at least four hours prior to measurement in order to reach a stable equilibrium. The dye solutions were carefully removed from the cells which were then washed with solvent and dried by aspiration prior to reuse.

The spectra of the Ni^{II}-TSPC solutions in N-methylformamide were obtained in the 520 to 700 nm region of the visible spectrum, by use of the Cary 14 recording spectrophotometer. Isosbestic points were found at $30^{\circ}C$ at 648 and 611 nm by super-imposing the spectra of 1.0×10^{-3}, 1.0×10^{-4}, 1.0×10^{-5}, and 1.0×10^{-6} M solutions in spectral cells of 0.01, 0.1, 1.0, and 10.0 cm path lengths, respectively, indicating the presence of an equilibrium in this concentration range (see Figure 2). The ionic strength of all the solutions were adjusted to a constant value by appropriate additions of $NaClO_4$ after the species in equilibrium were identified. The absorption spectra were then again obtained so that the equilibrium constant could be obtained for the system at a constant ionic strength of 1.6×10^{-3} M. The addition of $NaClO_4$ caused increased dye aggregation.

The absorption spectra of a 5.0×10^{-4} M solution of Ni^{II}-TSPC at natural ionic strength was carefully thermostated to 3°, 10°, and $20^{\circ}C$, so that the effect of temperature on the equilibrium could be studied (see Figure 3).

Figure 2.   Isosbestic Points by Varying Concentration

ABSORBANCE

WAVELENGTH (nm)

A — 1.0 X 10^{-3} M (0.01 cm cell)
B — 1.0 X 10^{-4} M (0.10 cm cell)
C — 1.0 X 10^{-5} M (1.0cm cell)
D — 1.0 X 10^{-6} M (10.0 cm cell)
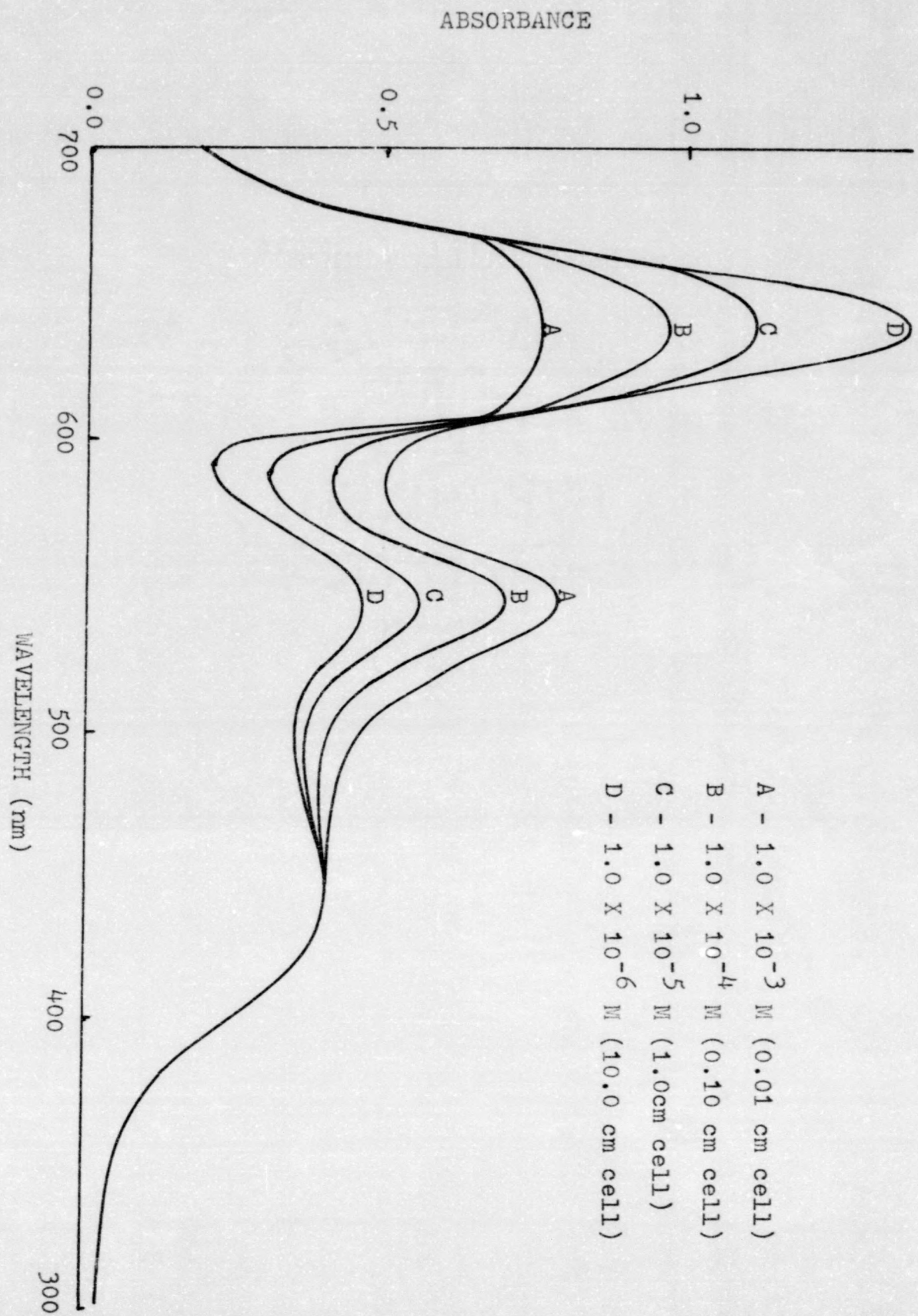
Figure 3.   Isosbestic Points of a 5.0×10^{-4} M Ni^{II}-TSPC
Solution at Different Temperatures

ABSORBANCE

WAVELENGTH (nm)

A — 5.0 X 10^{-4} M Ni^{II}-TSPC at 3°C

B — 5.0 X 10^{-4} M Ni^{II}-TSPC at 10°C

C — 5.0 X 10^{-4} M Ni^{II}-TSPC at 20°C
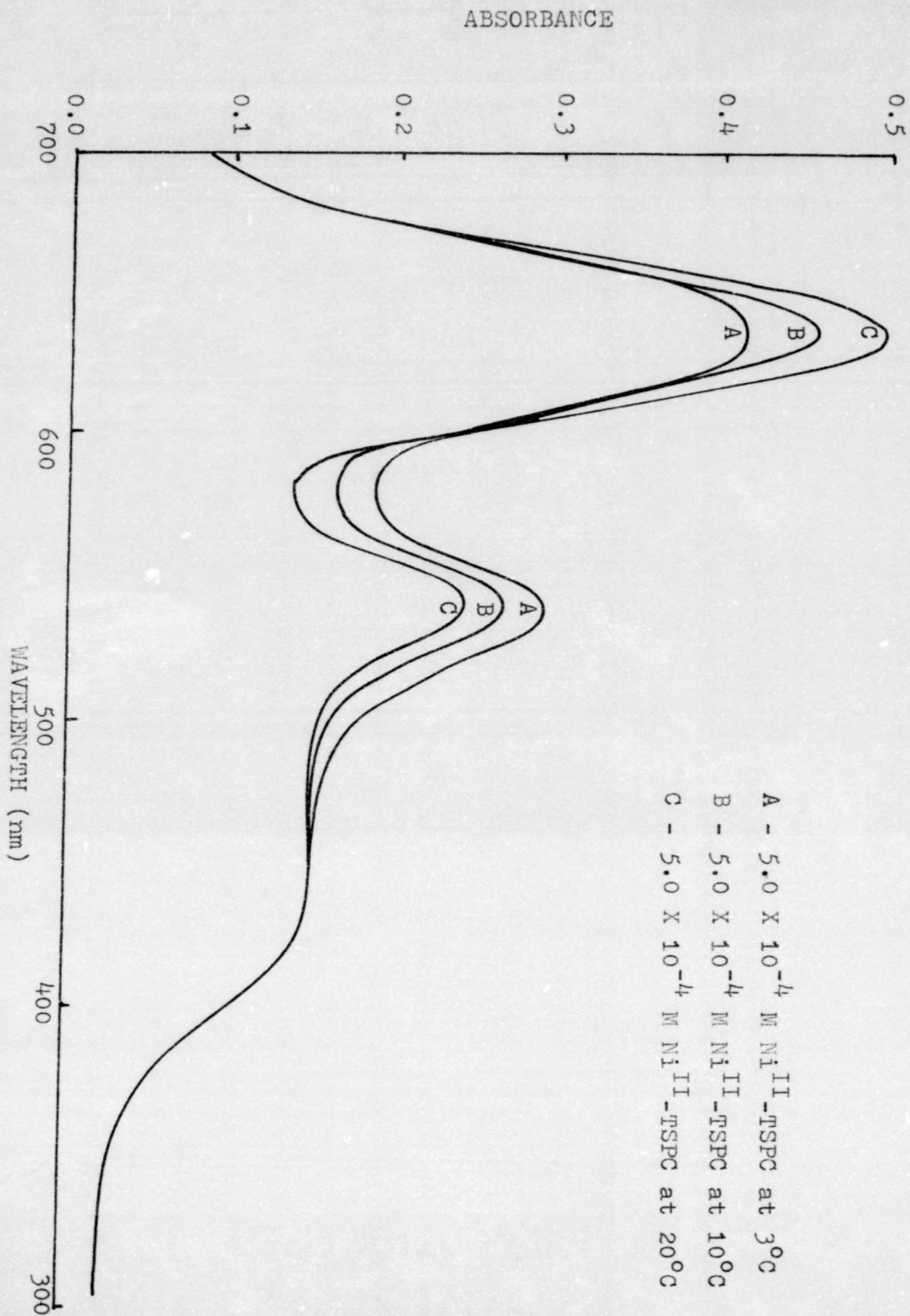
The effect of $NaClO_4$ was studied by obtaining the absorption spectra of a 1.0 X 10^{-4} M Ni^{II}-TSPC solution at 30°C after the addition of various amounts of the salt.

D. Preliminary Experiments

1. Nickel(II)-4, 4', 4", 4'"-tetrasulfophthalocyanine

A number of solubility tests on Ni^{II}-TSPC were run in various solvents (see Table 1) to determine the degree of solubility of the dye. After discovering several solvents in which the complex was quite soluble, an attempt was made to find the solvent in which the nickel (II) complex exhibited possible equilibrium conditions. This was accomplished by super-imposing absorption spectra of 1.0 X 10^{-6}, 1.0 X 10^{-5}, 1.0 X 10^{-4}, and 1.0 X 10^{-3} M solutions of Ni^{II}-TSPC using 10.0, 1.0, 0.1, and 0.01 cm path length spectral cells respectively. The spectra were obtained in the 520 to 700 nm region of the visible spectrum. Spectral shifts due to changes in temperature or addition of $NaClO_4$ were also observed.

a. Water

An attempt was first made to establish an equilibrium in water, but the spectra of a 1.0 X 10^{-6} M solution of Ni^{II}-TSPC gave a single broad peak at 615 nm with a slight shoulder at 662 nm. There were no other peaks present in the 520 to 700 nm region where the spectra were obtained. At higher concentrations of the dye, the shoulder disappeared leaving a broad band. This indicates that a high degree of aggregation of the dye occurs at concentrations above 1.0 X 10^{-6} M. Since such a high degree of polymerization occurs at low

Table 1

Solubility Table

	SOLVENT	DIELECTRIC CONSTANT	TEMP.(^{o}C)[*]	SOLUBILITY[**]
1.	Acetophenone	17.39	25	i
2.	Acetic Anhydride	20.7	19	i
3.	Acetonitrile	37.5	20	i
4.	Benzene	2.275	25	i
5.	Benzaldehyde	17.8	20	i
6.	Benzonitrile	25.20	25	i
7.	Carbon Tetrachloride	2.238	20	i
8.	Carbon Disulfide	2.641	20	i
9.	Chloronapthalene	5.04	25	i
10.	Chlorobenzene	5.621	25	i
11.	Dimethyl Sulfoxide	46.68	25	v
12.	1,4-Dioxane	2.209	25	i
13.	Ethyl Ether	4.335	20	i
14.	Ethyl Acetate	6.02	25	i
15.	Ethylene Carbonate	89.6	40	w
16.	Dimethylformamide	52.1	-40	v
17.	Formamide	111.0	20	v
18.	N-methylformamide	182.4	25	v
19.	Iodomethane	7.00	25	i
20.	Methanol	32.70	25	w
21.	Water	78.39	25	v
22.	Nitrobenzene	34.82	25	i
23.	Nitromethane	35.87	30	i

Table 1 (cont.)

	SOLVENT	DIELECTRIC CONSTANT	TEMP.(^{o}C)[*]	SOLUBILITY[**]
24.	Methyl Acetate	6.68	25	i
25.	Phenylacetonitrile	18.7	27	i
26.	Pyridine	12.4	21	i
27.	Tetrahydrofuran	7.58	25	i
28.	Trimethylphosphate			i
29.	Acetone	20.7	25	i
30.	Formic Acid	58.5	16	i
31.	Ethylenediamine	12.9	20	v
32.	Glycerol	42.5	25	s
33.	Ethylene Glycol	31.69	20	s
34.	Ethanol	24.55	25	i
35.	Pentyl Alcohol	13.9	25	i
36.	Tributylphosphate	7.959	30	i
37.	Sulpholane	43.3	30	i
38.	N-Methylpropionamide	172.2	25	s
39.	N-Methylacetamide	191.3	32	s
40.	N,N-Dimethylacetamide	37.78	25	w

* Dielectric constant temperature
** Solubility tests were carried out at room temperature.
v - very soluble (98 mg/10 ml); s - moderately soluble (49 mg/ml); w - weakly soluble; i - insoluble

concentrations of the complex, it would be difficult to obtain measurable equilibrium conditions.

b. Methanol

Due to the slight solubility of Ni^{II}-TSPC in methanol, it was impossible to prepare a series of solutions allowing the determination of the presence of an equilibrium. The spectra of the metal complex gave maxima at 675, 645, 612, and 344 nm. It was found that temperature changes had no effect on the relative heights of the maxima, thus indicating either the absence of an equilibrium or that temperature has little effect on the equilibrium. Upon addition of $NaClO_4$, the peaks at 675 and 645 nm disappeared, and a broad band appeared at 615 nm, indicating a shift to a higher polymeric form. No further studies were made of the effects of $NaClO_4$ on the aggregation of the dye complex in this solvent.

c. Ethylene Glycol

Ethylene glycol solutions of the Ni^{II}-TSPC dye were found to follow Beer's law producing identical spectra through the concentration range of 1.0×10^{-6} to 1.0×10^{-4} M. There were no shifts of maxima due to temperature changes, and the addition of $NaClO_4$ broadened the peak at 638 nm and shifted it toward shorter wavelengths while the intensity of the maximum at 671 nm decreased. This suggests formation of higher polymers.

d. Glycerol

Although Ni^{II}-TSPC is quite soluble in glycerol, no attempt was made to establish equilibrium between the species

of the complex in this solvent due to anticipated problems of concentration changes which might result from changes in the viscosity of the solvent when the temperature is varied.

e. N-Methylacetamide

The spectra of Ni^{II}-TSPC in N-methylacetamide contained maxima at 671, 644(shoulder), 604, and 343 nm. Spectra obtained on dye concentrations of 1.0 X 10^{-6} to 1.0 X 10^{-3} M exhibited no isosbestic points. Therefore, it was concluded that there was no common equilibrium present. Changes of temperature or the addition of $NaClO_4$ had no effect upon the absorption spectra of the dye, thus indicating that the solvent strongly favored a single species of the dye complex.

f. N,N-Dimethylacetamide

As in N-methylacetamide, solutions of the dye complex in N,N-dimethylacetamide were found to exhibit no conditions of equilibrium in concentrations of dye ranging from 1.0 X 10^{-6} to 1.0 X 10^{-3} M. Also, no changes were observed in the absorption spectra at various temperatures and at different concentrations of $NaClO_4$. The spectra of the complex appeared quite different in that there were only three maxima which occurred at 673, 508, and 300 nm. There was no maximum in the region of 644 nm and the broad band at 508 nm was nearly as intense as the 673 nm band.

g. N-Methylpropionamide

Solutions of the dye in N-methylpropionamide produced spectra very similar to that in N-methylacetamide. No common equilibrium was established in the concentration range of

1.0×10^{-6} to 1.0×10^{-3} M as evidenced by the absence of isosbestic points. No change was observed in the spectra either with variations in temperature or upon the addition of $NaClO_4$ to the solutions.

h. Hexamethylphosphoramide

Concentrations of the Ni^{II}-TSPC complex of 1.0×10^{-6} to 1.0×10^{-4} M in hexamethylphosphoramide were found to produce identical super-imposed spectra very similar to that of the dye in N-methylacetamide. Attempts to obtain spectral changes due to shifts in equilibrium between species of the dye by temperature variation and by the addition of $NaClO_4$ or TBHAP (tetrabutyl-hexammonium perchlorate) failed indicating the absence of an equilibrium.

i. Ethylenediamine

Attempts were made to determine if an equilibrium exists in Ni^{II}-TSPC solutions using ethylenediamine as a solvent. However, due to the corrosive nature of the solvent, the optical lens of the Cary 14 recording spectrophotometer became coated with a residue from the fumes, making it impossible to obtain measurements without purging the sample and reference compartments with N_2 gas. Due to the lack of available N_2 at the time, there were no further attempts to determine the presence of an equilibrium of the dye complex in ethylenediamine.

j. Dimethyl Sulfoxide

As with the cobalt(II) phthalocyanine complex, the attempted use of DMSO as a solvent for an equilibrium study

of Ni^{II}-TSPC proved futile.[18] Isosbestic points were found
to be absent in spectra obtained in a concentration range of
1.0×10^{-6} to 1.0×10^{-3} M, thus indicating the absence of a
common equilibrium. There were no spectral changes observed
with changes in temperature or with the addition of $NaClO_4$.
Maxima were found at wavelengths of 673, 644(shoulder), 600,
and 332 nm.

k. Ethylene Carbonate

No attempt was made to determine the presence of an
equilibrium between different species of the dye in ethylene
carbonate, since spectral measurements would have to be made
at elevated temperatures due to the high freezing point of
the solvent.

l. Dimethylformamide

The super-imposed absorption spectra of 1.0×10^{-3} to
1.0×10^{-6} M Ni^{II}-TSPC solutions gave identical spectra indi-
cating the absence of equilibrium between species of the dye.
Changes in temperature effected no change in the spectra, but
the addition of $NaClO_4$ caused the maxima at 644 nm to disap-
pear. There was a significant decrease in the intensity of
the 671 nm peak as a broad band appeared at the 608 nm maxi-
mum, indicating a shift to a higher polymeric form.

m. Formamide

The spectra of the Ni^{II}-TSPC dye complex had maxima at
670, 638, 606, and 338 nm in formamide. Solutions of the dye
in formamide showed shifts in the relative peak heights at
positions 670 and 638 nm due to changes in concentration.

However, an attempt was not made to determine the concentration range where isosbestic points could be obtained. With increased concentration, the peak at 638 nm grew while the peak at 670 nm decreased, and when the concentration of the dye was decreased the converse occurred. This indicated the presence of an equilibrium between two or more species of the dye. The maximum molar absorptivities for the monomeric species were found by driving the equilibrium completely in favor of the monomer with increasing dilution and higher temperatures. The molar absorptivities obtained for the single species were 3.47×10^4 $M^{-1}cm^{-1}$ at 638 nm and 1.73×10^5 $M^{-1}cm^{-1}$ at 670 nm. Unfortunately, all of the available formamide was used before isosbestic points or the dimer molar absorptivity were determined.

RESULTS AND DISCUSSION

The results presented in this section of the thesis include the types of species present in equilibrium over a concentration range of 1.0×10^{-3} to 1.0×10^{-6} M in Ni^{II}-TSPC, their molar absorptivities at the respective absorption maxima, concentration quotients at various concentrations of Ni^{II}-TSPC, the association constant obtained either by extrapolating the concentration quotients to infinite dilution or by activity coefficient correction, and the degree of ion association. The effects of salt $(NaClO_4)$ and changes in temperature are also discussed, and the values of the thermodynamic parameters are compared with analogous systems in water.

A. <u>Determination of Species Present in Common Equilibrium</u>

Since isosbestic points were found at 648 and 611 nm for super-imposed spectra of 1.0×10^{-3}, 1.0×10^{-4}, 1.0×10^{-5}, and 1.0×10^{-6} M solutions of Ni^{II}-TSPC in N-methylformamide, the presence of a common equilibrium was indicated. Therefore, the first problem became the establishment of the number and kind of species present within the common equilibrium concentration range. This was done using a method by Kuhn et al.[28] which was applied in a metal-free phthalocyanine sulphonate system. Assuming the existence of an equilibrium

27

between monomer (M) and aggregate (M_n) with only one kind of association, the following equations become applicable.

$$nM = M_n, \text{ where } Q = M_n/M^n \tag{1}$$

$$C = M + nM_n \tag{2}$$

$$CE = ME_M + M_nE_n, \; E_n = A/Cd \tag{3}$$

where n is the degree of aggregation; C is the total concentration of Ni^{II}-TSPC; A is the absorbance of the solutions at a given wavelength; d is the path length of the cell; Q is the concentration quotient; E, E_M, and E_n are the molar absorptivity of the mixture, monomer, and aggregate, respectively at that wavelength. Use of the method described by Kuhn and coworkers allows the combination of equations 1-3 to give equation 4:

$$y = 1/n(x) + a \tag{4}$$

where

$$y = \left[\log \; C(E - E_n/n)\right]$$
$$x = \left[\log \; C(E_n - E)\right]$$

and

$$a = (1 - 1/n) \log (E_M - E_n/n) - 1/n \log (nQ) \tag{5}$$

with x and y determined from E_M and E_n as well as from the absorbance of the different Ni^{II}-TSPC concentrations provided they are known. Since diluting and heating favors the monomer, these techniques were used to shift the equilibrium in favor of the monomer in order to determine its molar absorptivity at 668 nm. However, the slow equilibration of the

solutions with changes in temperature makes this difficult.
Therefore, the value for E_M was obtained by extrapolation to
infinite dilution as described in the literature.[3] The val-
ues obtained for E_M on aged solutions within the common equi-
librium (see Table 2) are plotted in Figure 4. A value of
1.78×10^5 $M^{-1}cm^{-1}$ was obtained for E_M. Since larger poly-
meric species are favored at high concentrations, the value
of E_n was obtained by extrapolation of E at infinite concen-
tration or where the reciprocal of the total concentrations
of Ni^{II}-TSPC is zero as shown in Figure 5. If it is assumed
that the degree of aggregation is two, a value of 7.64×10^4
$M^{-1}cm^{-1}$ is obtained for E_n.

Once the values for E_n and E_M were obtained as well as
the molar absorbance and absorptivity of the different mix-
ture concentrations for several solutions within the equili-
brium (see Tables 3 and 4), the values for x and y were
obtained (see Tables 5 and 6). Figure 6 shows a plot of x
vs. y over a concentration range of 1.0×10^{-3} to 1.0×10^{-6}
M at 668 nm and $30^\circ C$. The plot was linear throughout the
concentration range with a slope of $1/n$ (from equation 4).
Substitution of $1/n$ back into equation 5 allows the concen-
tration quotient to be calculated. A value of 2.08 was
obtained for n, indicating that the degree of aggregation is
two which agrees with the assumption made. A value of 2.90
$\times 10^3$ M^{-1} was found for Q upon substitution of $1/n$ back into
equation 5.

TABLE 2

Measurement of the Absorbance at Different Dye Concentrations

C_T (M)	ABSORBANCE*	LOG E	LOG (C_T X 10^7)
1.0 X 10^{-3}	83.00	4.9191	4.0000
5.0 X 10^{-4}	49.00	4.9912	3.6990
1.0 X 10^{-4}	13.60	5.1303	3.0000
5.0 X 10^{-5}	7.57	5.1801	2.6990
1.0 X 10^{-5}	1.70	5.2304	2.0000
5.0 X 10^{-6}	0.87	5.2415	1.6990
1.0 X 10^{-6}	0.18	5.2499	1.0000

* Absorbance measurements were made at 668 nm and 30°C.

Figure 4. Extrapolation of E to Infinite Dilution for the

Determination of E_M

LOG E

5.1495

5.0343

4.9191

● LOG E_M = 5.2504
E_M = 1.78 X 10^5 M^{-1} cm^{-1}

1.0

2.0

3.0

4.0

LOG (C_T X 10^7)
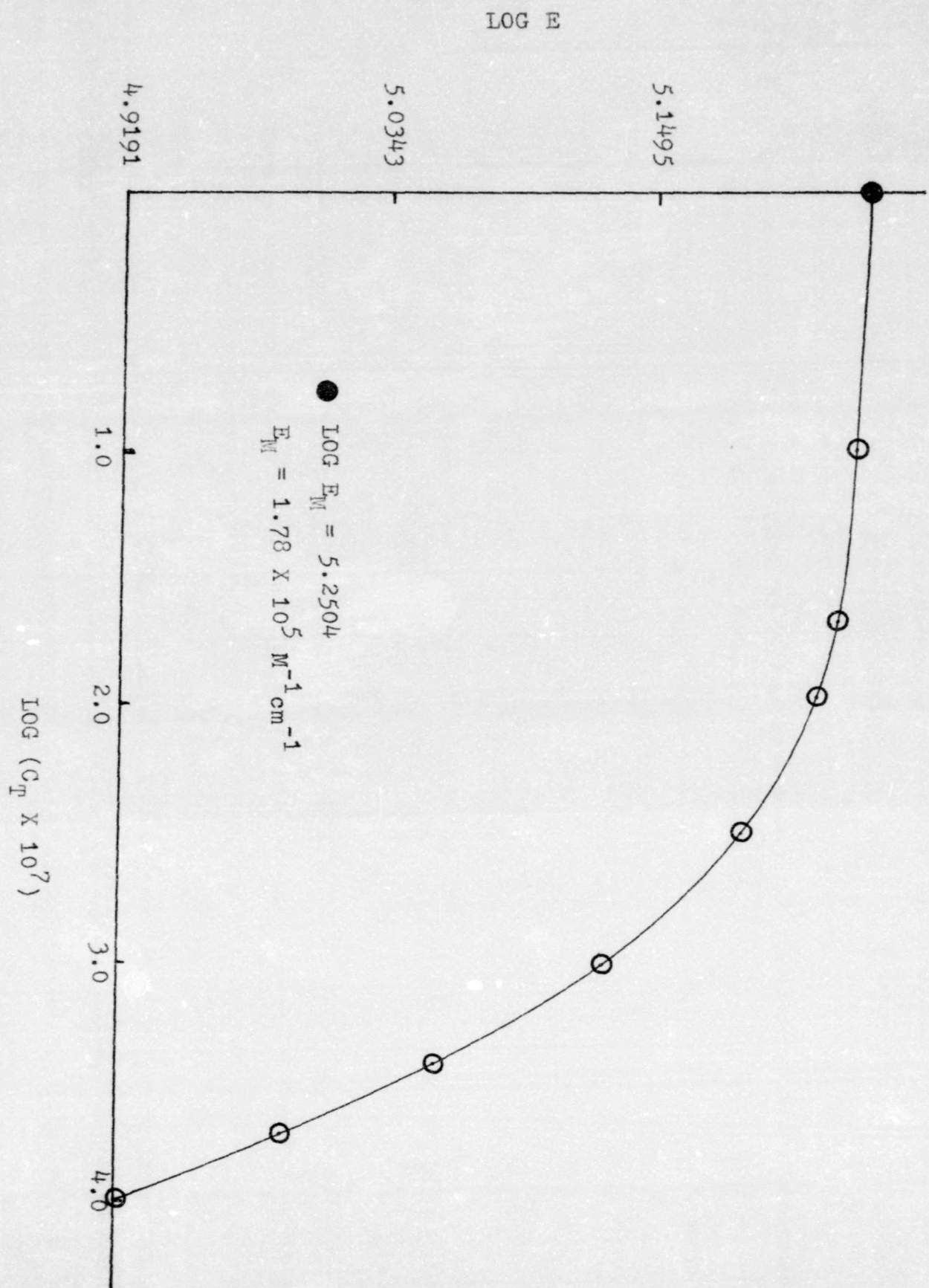
Figure 5. Extrapolation of E_n vs. $1/C_T$ to Infinite Concentration for Determination of E_D

LOG E_n

LOG (1/T x 10^{-2})

● LOG E_D = 4.8832
E_D = 7.64 X 10^4 M^{-1} cm^{-1}
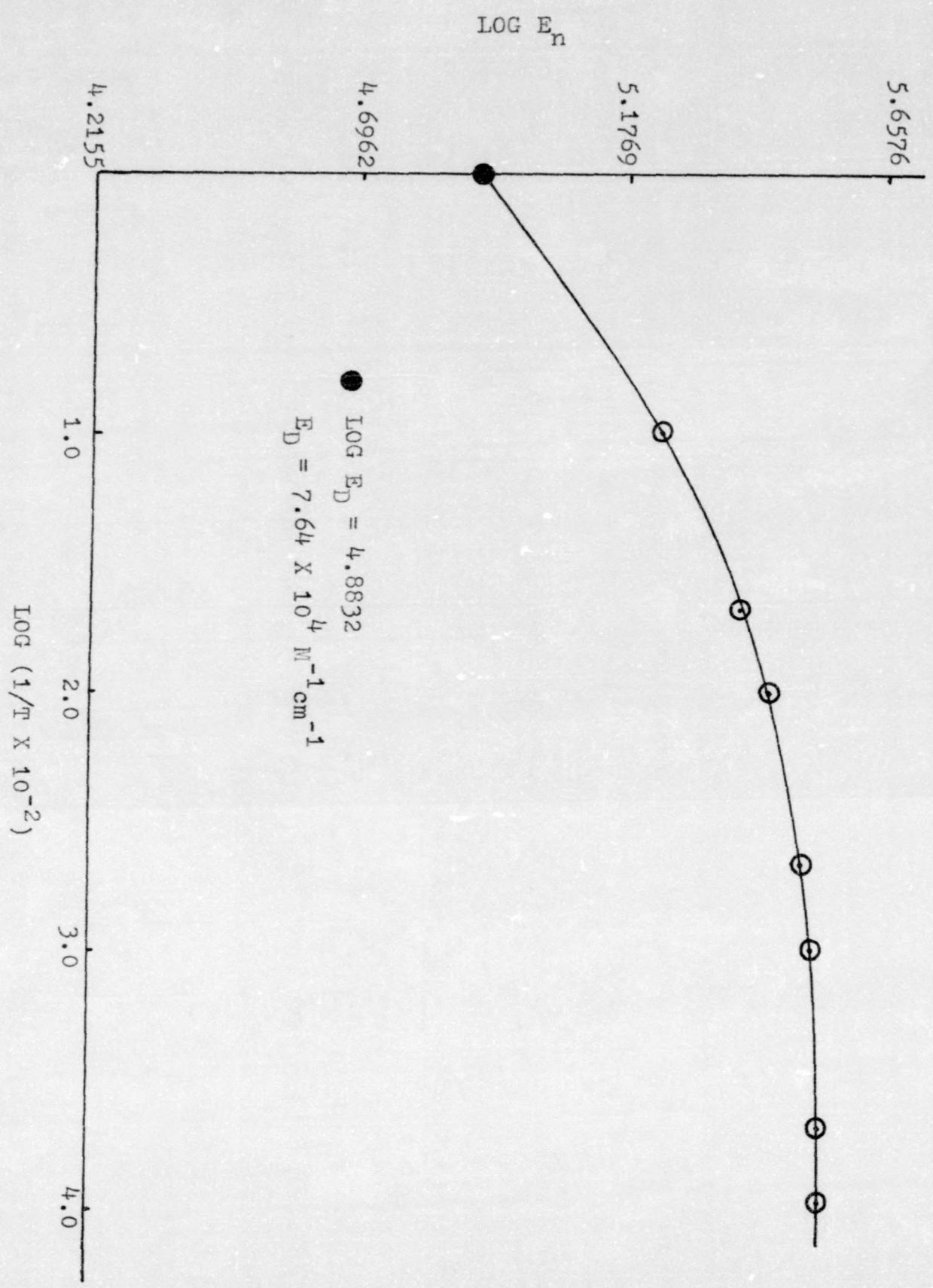
TABLE 3

Absorbance and Optical Absorptivities of Different Ni^{II}-TSPC
Concentrations

C_T (M)	ABSORBANCE*	LOG E_n	LOG $(1/C \times 10^{-2})$
1.0×10^{-3}	83.00	5.2201	1.0000
5.0×10^{-4}	49.00	5.2923	1.3010
1.0×10^{-4}	13.60	5.4330	2.0000
5.0×10^{-5}	7.57	5.4811	2.3010
1.0×10^{-5}	1.70	5.5315	3.0000
5.0×10^{-6}	0.87	5.5426	3.3010
1.0×10^{-6}	0.18	5.5509	4.0000

* Absorbance measurements were made at 668 nm and $30^{\circ}C$.

TABLE 4

Determination of the Molar Absorptivity of Dye Solutions

C_T (M)	ABSORBANCE	E ($M^{-1}cm^{-1}$)
1.0×10^{-3}	83.00	8.30×10^4
5.0×10^{-4}	49.00	9.80×10^4
1.0×10^{-4}	13.60	1.36×10^5
5.0×10^{-5}	7.57	1.51×10^5
1.0×10^{-5}	1.70	1.70×10^5
5.0×10^{-6}	0.87	1.75×10^5
1.0×10^{-6}	0.18	1.78×10^5

TABLE 5

Values of x and y for Assumed Monomer-Dimer Equilibrium

C_T (M)	x	y
1.0×10^{-3}	1.9777	1.6515
5.0×10^{-4}	1.6021	1.4757
1.0×10^{-4}	0.6732	0.9903
5.0×10^{-5}	0.1303	0.7513
1.0×10^{-5}	- 1.0967	0.1199
5.0×10^{-6}	- 1.8239	- 0.1649
1.0×10^{-6}	- 3.0000	- 0.8539

TABLE 6

Values of x and y for Assumed Dimer-Tetramer Equilibrium

C_T (M)	x	y
1.0×10^{-3}	2.4362	0.8195
5.0×10^{-4}	2.1106	1.0334
1.0×10^{-4}	1.3424	0.7752
5.0×10^{-5}	1.0107	0.5717
1.0×10^{-5}	0.2695	- 0.0284
5.0×10^{-6}	- 0.0434	- 0.3072
1.0×10^{-6}	- 0.7496	- 0.9935

Figure 6. Plot of x vs. y for Assumed Monomer-Dimer
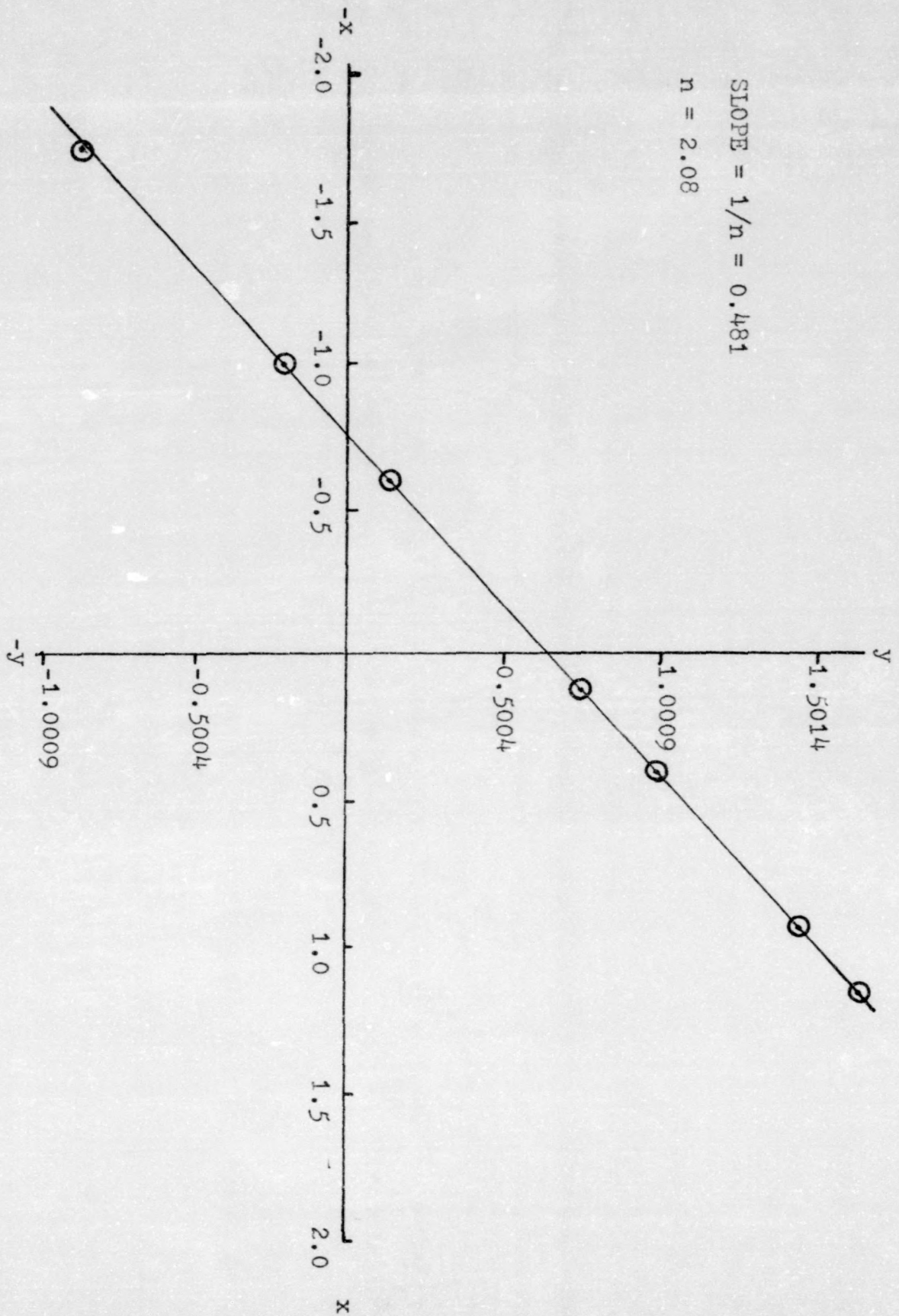
Equilibrium

To determine whether there are other equilibria plausible, a dimer-polymer equilibrium was assumed and Beer's law values of E_D and E_n were calculated where n was assumed to be two. The E_D and E_n values calculated for dimer and tetramer are $3.56 \times 10^5 \ M^{-1}cm^{-1}$ and $1.53 \times 10^5 \ M^{-1}cm^{-1}$, respectively. The values of x and y were then calculated and plotted as shown in Figure 7. The degree of aggregation, n, was found to be 0.95, thus indicating that there is no dimer-tetramer equilibrium, since a value of 2.0 was required for n. The possibility of a higher polymer equilibrium was ruled out since it has been shown previously[8] that organic solvents favor the monomeric species in equilibria involving tetra-sulfonated metallophthalocyanine systems. Therefore, the equilibrium is indeed one involving the monomer and dimer species.

B. The Determination of the Association Constant

Table 7 shows typical values of the monomer-dimer concentration quotients, Q, calculated from the absorbance of different Ni^{II}-TSPC concentrations at $30^{o}C$ and natural ionic strength. Extrapolation of Q to infinite dilution yields a value of $K = 2.89 \times 10^3 \ M^{-1}$ (see Figure 8) since

$$\lim \frac{f_D}{f_M^2} = 1, \text{ hence } \lim Q = K = \frac{C_D}{C_M^2} \frac{f_D}{f_M^2} = \frac{C_D}{C_M^2} \tag{6}$$

where

$$C_M = \frac{2A - E_D C_T}{2E_M - E_D}$$

Figure 7.   Plot of x vs. y for Assumed Dimer-Tetramer

Equilibrium
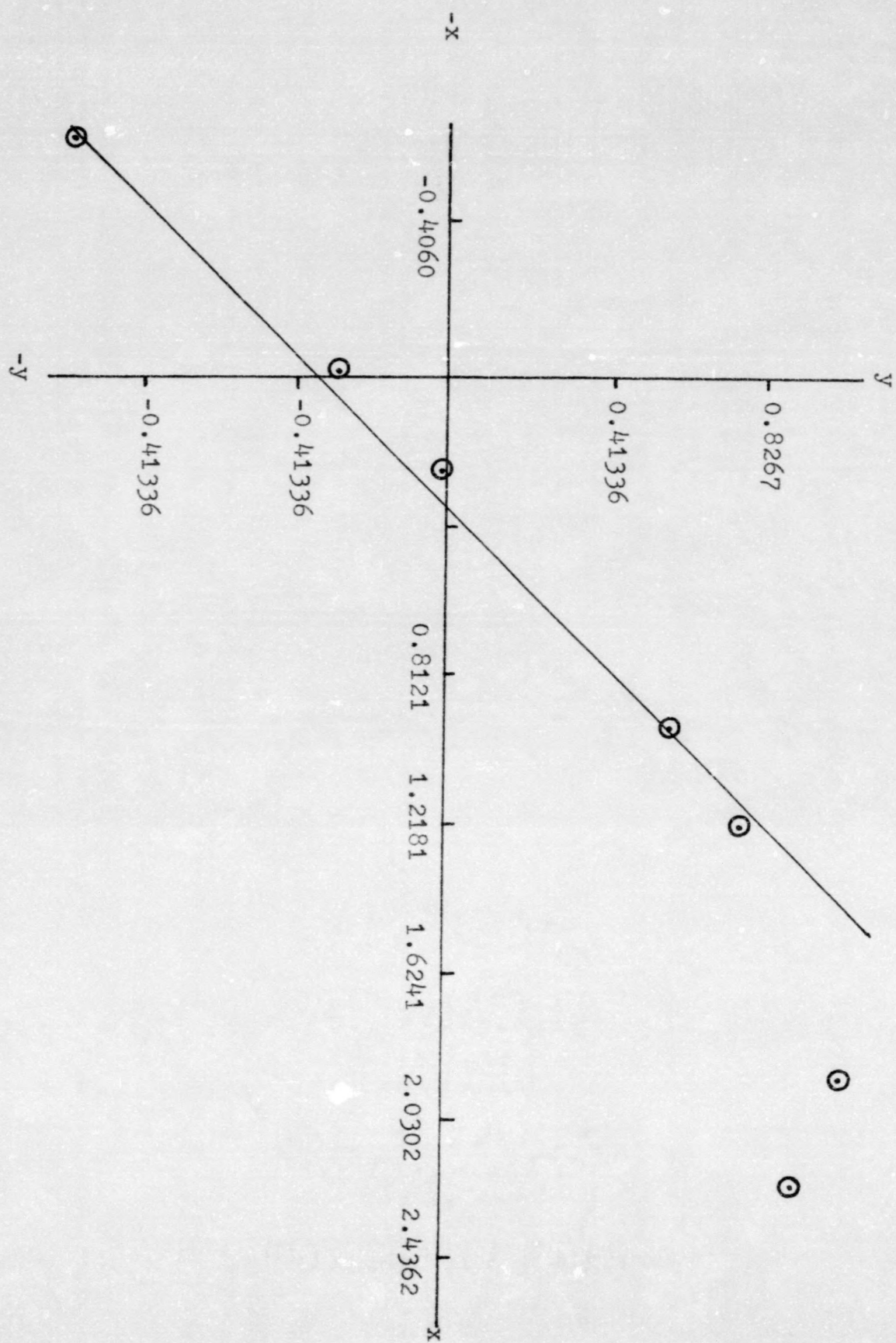
TABLE 7

Concentration Quotients at Different Dye Concentrations

C_T (M)	C_M (M)	C_D (M)	Q (M^{-1})
1.0×10^{-3}	3.20×10^{-4}	3.40×10^{-4}	3.31×10^{3}
5.0×10^{-4}	2.14×10^{-4}	1.43×10^{-4}	3.13×10^{3}
1.0×10^{-4}	7.00×10^{-4}	1.50×10^{-5}	3.07×10^{3}
5.0×10^{-5}	4.04×10^{-5}	4.79×10^{-6}	2.94×10^{3}
1.0×10^{-5}	9.43×10^{-6}	2.86×10^{-7}	3.22×10^{3}
5.0×10^{-6}	4.86×10^{-6}	6.79×10^{-8}	2.87×10^{3}
1.0×10^{-6}	9.97×10^{-7}	2.86×10^{-9}	2.88×10^{3}

Figure 8.   Determination of K by Extrapolation of Q to
Infinite Dilution

LOG Q

● LOG K = 3.46
K = 2.89 X 10³ M⁻¹

LOG (C_T X 10⁷)
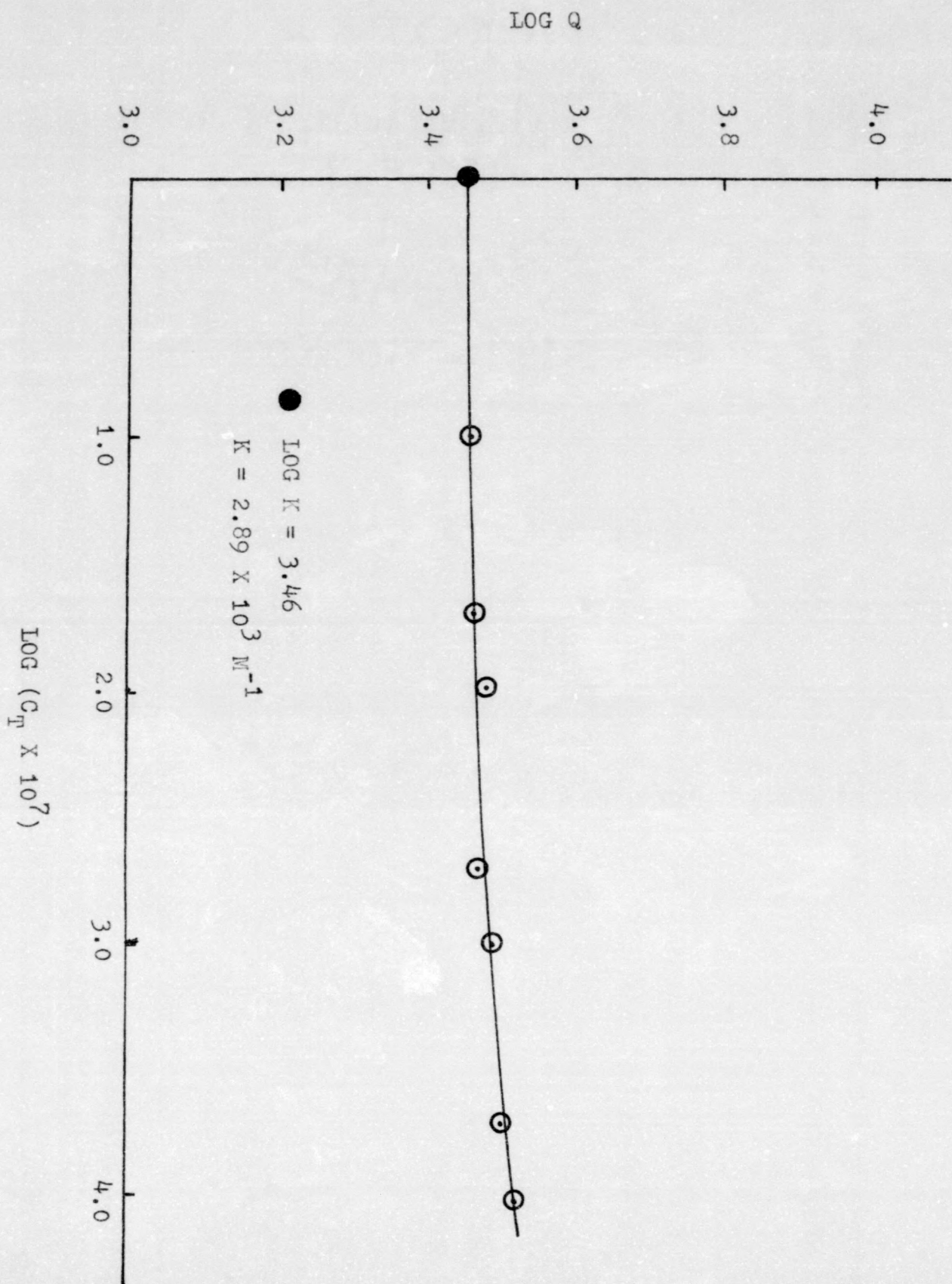
and

$$C_D = \frac{C_T - C_M}{2}$$

with f_M and f_D representing the activity coefficients of the monomeric and dimeric species, respectively.

C. Calculation of Charges on Monomer and Dimer Species

Substitution of the Debye-Huckel limiting law[29] into equation 6 gives

$$\log K = \log Q + 0.15(u)^{1/2} \, 2(z_M)^2 - (z_D)^2 \qquad (7)$$

and

$$u = 1/2 \left[(4C_T) + C_M(z_M)^2 + C_D(z_D + n)^2 - n(C_D) \right] \qquad (8)$$

where u is the ionic strength; n is the degree of ion pairing between Na^+ and the dimer; C_M and C_D are the concentrations of monomer and dimer; z_M and z_D are the charges on the monomer and dimer, respectively. Equation 7 allows corrections to be made for changes in ionic strength and assumes that ion pairing occurs with the greater charged dimeric species only. Therefore, the association constant, K, can be determined from corrected values of Q for all concentrations within the common equilibrium if the ionic strengths and the charges on the monomer and dimer are known.

Table 8 shows the K values obtained for various concentrations of Ni^{II}-TSPC within the common equilibrium assuming no ion pairing, where the charges for the monomer and dimer are -4 and -8, respectively. From the values of K shown, it can be seen that the charges are different from those assumed

TABLE 8

K Values for -4 and -8 Respective Charges on Monomer and Dimer

C_T (M)	u (M)	Q (M^{-1})	K (M^{-1})
1.0×10^{-3}	1.54×10^{-2}	3.31×10^3	8.41×10^2
5.0×10^{-4}	7.29×10^{-3}	3.13×10^3	1.22×10^3
1.0×10^{-4}	1.24×10^{-3}	3.07×10^3	2.08×10^3
5.0×10^{-5}	5.70×10^{-4}	2.94×10^3	2.26×10^3
1.0×10^{-5}	1.04×10^{-4}	3.22×10^3	2.88×10^3
5.0×10^{-6}	5.10×10^{-5}	2.87×10^3	2.65×10^3
1.0×10^{-6}	1.01×10^{-5}	2.88×10^3	2.78×10^3

since the values of K are not constant throughout the equilibrium concentration range. Therefore, since differences in ionic strength have been compensated for, ion pairing must occur, or the equations do not hold for highly charged ions. If we assume that ion pairing occurs and that the charges are -4 and -7 for monomer and dimer, respectively, we can see from Table 9 that a constant value of K is still not attained throughout the equilibrium concentration range. The values of K obtained increase at higher dilution, thus indicating by equation 7 a greater degree of ion association than that assumed. Therefore, assuming a still greater degree of ion pairing where the charges of monomer and dimer are assumed to be -4 and -6, respectively, values of K at different concentrations of Ni^{II}-TSPC are almost constant. This occurs throughout a concentration range of 1.0×10^{-3} to 1.0×10^{-6} M as shown in Table 10. Table 11 shows that the assumption of -4 and -5 charges for monomer and dimer, respectively, again causes great differences to appear in the values of K which decrease at lower dye concentrations. This indicates a lesser degree of ion pairing than that assumed. Therefore, the charges on the species are believed to be -4 and -6 for the monomer and dimer, respectively, and the correction of concentration quotients for ion pairing and ionic strength gives an average value of $2.86 \pm 0.02 \times 10^3$ M^{-1} for K. This in good agreement with the value of 2.89×10^3 M^{-1} obtained for K by extrapolation of Q to infinite dilution, and with 2.90×10^3 M^{-1} obtained by substitution of 1/n and the y

TABLE 9

K Values for -4 and -7 Respective Charges on Monomer and Dimer

c_T (M)	u (M)	Q (M^{-1})	K (M^{-1})
1.0×10^{-3}	1.27×10^{-2}	3.31×10^3	1.72×10^3
5.0×10^{-4}	6.14×10^{-3}	3.33×10^3	1.98×10^3
1.0×10^{-4}	1.12×10^{-3}	3.07×10^3	2.52×10^3
5.0×10^{-5}	5.36×10^{-4}	2.94×10^3	1.91×10^3
1.0×10^{-5}	2.04×10^{-4}	3.22×10^3	2.96×10^3
5.0×10^{-6}	5.05×10^{-5}	2.87×10^3	2.75×10^3
1.0×10^{-6}	1.00×10^{-5}	2.88×10^3	2.83×10^3

TABLE 10

K Values for -4 and -6 Respective Charges on Monomer and Dimer

C_T (M)	u (M)	Q (M^{-1})	K (M^{-1})
1.0×10^{-3}	1.03×10^{-2}	3.31×10^3	2.88×10^3
5.0×10^{-4}	5.14×10^{-3}	3.13×10^3	2.84×10^3
1.0×10^{-4}	2.03×10^{-3}	3.07×10^3	2.88×10^3
5.0×10^{-5}	5.05×10^{-4}	2.94×10^3	2.85×10^3
1.0×10^{-5}	8.62×10^{-5}	3.22×10^3	2.84×10^3
5.0×10^{-6}	5.00×10^{-5}	2.87×10^3	2.85×10^3
1.0×10^{-6}	1.00×10^{-5}	2.88×10^3	2.88×10^3

TABLE 11

K Values for -4 and -5 Respective Charges on Monomer and Dimer

C_T (M)	u (M)	Q (M^{-1})	K (M^{-1})
1.0×10^{-3}	8.76×10^{-3}	3.31×10^3	4.15×10^3
5.0×10^{-4}	4.29×10^{-3}	3.13×10^3	3.67×10^3
1.0×10^{-4}	9.25×10^{-4}	3.07×10^3	3.31×10^3
5.0×10^{-5}	4.78×10^{-4}	2.94×10^3	3.10×10^3
1.0×10^{-5}	1.98×10^{-4}	3.22×10^3	3.11×10^3
5.0×10^{-6}	4.97×10^{-5}	2.87×10^3	2.92×10^3
1.0×10^{-6}	1.00×10^{-5}	2.88×10^3	2.90×10^3

intercept into equation 5. Thus, an average value of $K = 2.88 \pm 0.02 \times 10^3 \, M^{-1}$ is obtained for the monomer-dimer equilibrium. Similar analysis involving ion pairing with the monomer species were unsuccessful in that the association constants were inconsistent.

The equilibrium constant obtained for the above monomer-dimer equilibrium of Ni^{II}-TSPC in N-methylformamide is inconsistent with equilibrium constants reported for other phthalocyanines in water and nonaqueous solvents (see Table 12). For example, the reported value of $K = 1.58 \times 10^4 \, M^{-1}$ for Cu^{II}-TAPC in benzene is nearly four orders of magnitude lower than that of Cu^{II}-TSPC in water, a solvent of much greater dielectric constant. The dominant role of water as the solvent in the latter system, no doubt is associated with the reduction of repulsive forces between the similarly charged dye anions in the aggregate. Moreover, the strong solvent-solvent interaction excludes the dye molecules from solution and enhances the formation of an aggregate. In this study, the low equilibrium constant for the dimerization of Ni^{II}-TSPC suggests that solvation interferes with aggregation despite the high dielectric constant of N-methylformamide which would reduce the repulsive forces between the Ni^{II}-TSPC anions. From Table 1 we find that the dielectric constant of N-methylformamide (182.4 at $25^\circ C$) is much greater than that of water (78.39 at $25^\circ C$). However, the solvent-solvent interaction is quite different from water due to the difference in the hydrogen bonding properties of the two solvents

TABLE 12

Dimerization Constants of Several Phthalocyanine Dye Systems

COMPLEX	SOLVENT	LOG K[*]
Fe^{III}-TSPC	H_2O	7.11 ± 0.04
H_2TSPC	H_2O	7.79
	50% EtOH : H_2O	6.78
Co^{II}-TSPC	H_2O	5.47 ± 0.09
Cu^{II}-TSPC	H_2O	8.14
Cu^{II}-TAPC[**]	Benzene	4.20
	CCl_4	6.47
$(VO)^{II}$-TSPC	H_2O	6.70
$(VO)^{II}$-TAPC	Benzene	6.04

* K was determined at 25^oC and at natural ionic strength
except for $(VO)^{II}$-TSPC in H_2O, where u = 0.006.

** Tetraalkylphthalocyanine dye containing the R group
$-SO_2NH(CH_2)_{17}CH_3$

where water has two available hydrogens per molecule while N-methylformamide has only one.

On the other hand, the results of this study are consistent with the observations of Monahan et al.[16] who examined the monomer-dimer equilibrium of Cu^{II}-TAPC in several nonaqueous solvents and found that the aggregation tendency of the dye is diminished as the dielectric constant of the solvent increased. The order of decreasing phthalocyanine dye dimerization in the several solvents was: $CCl_4 >$ benzene $>$ toluene $>$ chloroform $>$ dioxane $>$ DHF $>$ THF. It was concluded that in order to form the dimer, the dye-dye interaction must be strong enough to overcome any other forces favoring solvation of the monomer. Thus, as the dielectric constant of the solvent is increased, the screening of the dye-dye interaction by the solvent becomes more efficient. This is found to be true in this system despite the reduction in the repulsive forces between Ni^{II}-TSPC anions. Hence, dimerization is not very favorable in N-methylformamide.

As has been the case in many other studies on the aggregation of phthalocyanine dye complexes, the addition of salt causes a shift to favor the dimer species. This has been attributed to the increased ion pairing brought on by the increase in ionic strength upon the addition of salt.[2,3,5]

As higher temperatures are attained, the monomer-dimer equilibrium is shifted toward higher concentrations of monomer. This is evidenced by the spectra shown in Figure 3. When a total concentration of 5.0×10^{-6} M in dye is reached,

the equilibrium is no longer shifted toward the monomer when the temperature is increased. However, sufficient cooling causes a decrease in monomer and shifts the equilibrium toward the dimer species.

D. Determination of Thermodynamic Properties

Using the equation, ΔG^o = -RT ln K, a value of -4.79 $\pm$ 0.02 kcal/mole was obtained for ΔG^o. The effects of temperature on the equilibrium are shown in Figure 3, and these values are used in the calculation of the thermodynamic properties. The relationship between temperature and the association constant is given by a variation of the Gibbs-Helmholtz equation[29] where

$$\log K = \frac{-\Delta H^o}{2.303 \ RT} + C' \tag{9}$$

A plot of log K vs. 1/T will yield a straight line if ΔH^o is independent of temperature. The slope of the linear plot is equal to $-\Delta H^o/2.303$ RT from which ΔH^o can be determined. Figure 9 is a plot of log K at 3°, 10°, and 20^oC for a 5.0 X 10^{-4} M solution of Ni^{II}-TSPC vs. reciprocal temperature. A linear plot was obtained indicating ΔH^o is independent of temperature. From the slope of the plot a value of -6.22 kcal/mole was found for ΔH^o. A value of -4.74 e.u. was obtained for ΔS^o at 668 nm and 30^oC using the Gibbs free energy relationship, $\Delta G^o = \Delta H^o - T\Delta S^o$.

A comparison of the thermodynamic parameters obtained for the dimerization of Ni^{II}-TSPC in N-methylformamide is made with those determined in water for the Co^{II}-TSPC and

Figure 9.   Determination of ΔH^o

LOG K

1/T X 10³
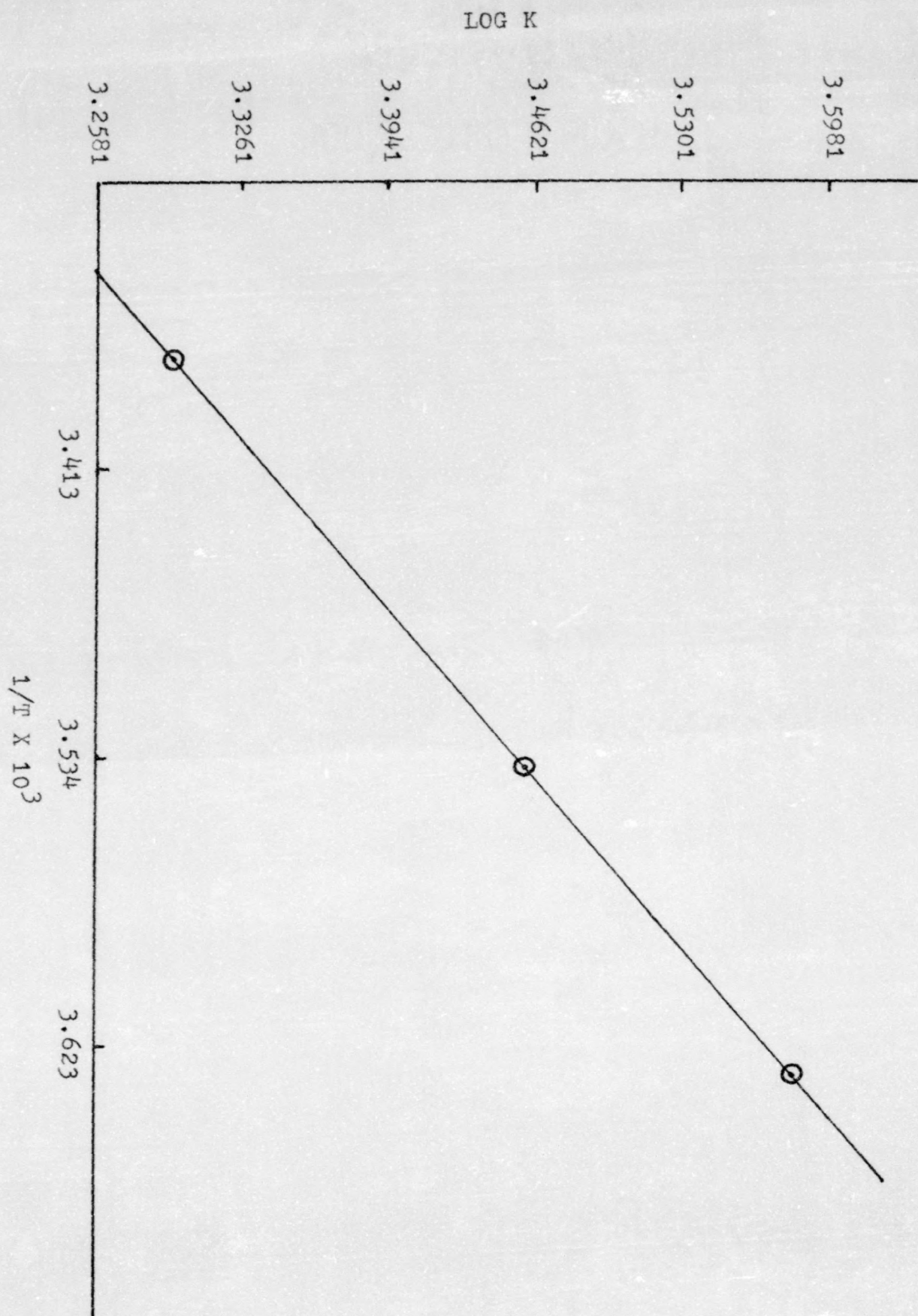
Cu^{II}-TSPC systems (see Table 13). The less negative value for the ΔH^o of the Ni^{II}-TSPC system indicates that the binding forces between monomeric species forming the dimer are weaker than those in the aqueous Co^{II}-TSPC and Cu^{II}-TSPC systems. Consequently, this would lead to a smaller dimerization constant which was obtained. The negative ΔG^o values obtained for all systems indicate that dimerization is favorable in all three systems.

TABLE 13

Thermodynamic Parameters for Ni^{II}-TSPC in N-Methylformamide
and Aqueous Co^{II}-TSPC and Cu^{II}-TSPC Systems

	Ni^{II}-TSPC	Co^{II}-TSPC	Cu^{II}-TSPC
ΔH^o	-6.2 kcal/mole	-14.0 kcal/mole	-13.4 kcal/mole
ΔG^o	-4.8 kcal/mole	- 8.0 kcal/mole	-10.0 kcal/mole
ΔS^o *	-4.7 e.u.	-18.0 e.u.	-10.9 e.u.

* ΔS^o values were determined at 25, 30, and 38°C for
Cu^{II}-TSPC, Ni^{II}-TSPC and Co^{II}-TSPC, respectively.

```
 1 PRINT "DETERMINATION OF MONOMER-DIMER ASSOCIATION CONSTANT"

 5 INPUT "MONOMER EXTCT. COEFF.="M, "DIMER EXTCT. COEFF.="D

10 INPUT "N+ =F, "M+ ="G, "P+ ="H

15 INPUT "A="A, "C(T)="T,

20 PRINT "C(T)", "C(M)", "C(D)", "Q","CLG(K)"

25 LET X = (2*A-D*T)/(2*M-D)

30 LET Y = (T-X)/(2)

35 LET Q = (T - X)/(2 * X↑2)

40 LET I = 0.5(F↑2*4*T + G↑2*X + H↑2*Y - 2*Y)

45 LET P = SQR(I)

50 LET Z = CLG(Q) + 0.15*P*(2*G↑2 - H↑2)

55 PRINT T,X,Y,Q,Z

60 PRINT

65 PRINT "I ="I

70 PRINT

75 PRINT

80 GO TO 15

85 END
```

```
 1 PRINT "DETERMINATION OF DIMER-TETRAMER ASSOCIATION CONSTANT"

 5 INPUT "DIMER EXTCT. COEFF. ="M, "TETRAMER EXTCT. COEFF. ="D

10 INPUT "N+ ="F, "M+ ="G, "P+ ="H

15 INPUT "A="A, "C(T) ="T

20 PRINT "C(T)","C(M)","C(D)","Q","CLG(K)"

25 LET X = (2*A-D*T)/(2*M-D)

30 LET Y = (T-X)/2

35 LET Q = (T-X)/(2*X↑2)

40 LET I = 0.5(F↑2*4*T + G↑2*X + H↑2*Y - 2*Y)

45 LET P = SQR(I)

50 LET Z = CLG(Q) + 0.15*P*(2*G↑2 - H↑2)

55 PRINT T,X,Y,Q,Z

60 PRINT

65 PRINT "I ="I

70 PRINT

75 PRINT

80 GO TO 15

85 END
```

BIBLIOGRAPHY

1. K. Fenkart and C. H. Brubaker, Jr., J. Inorg. Nucl. Chem., 30, 3245 (1968).

2. U. Ahrens and H. Kuhn, Z. Phys. Chem. (Frankfurt and Main), 37, 1 (1963).

3. Z. A. Schelly, R. D. Farina and E. M. Eyring, J. Phys. Chem., 74, 617 (1970).

4. Z. A. Schelly, D. J. Harward, P. Hemmes and E. M. Eyring, J. Phys. Chem., 74, 3040 (1970).

5. R. D. Farina, D. J. Halko, and J. H. Swinehart, J. Amer. Chem. Soc., 76, 2343 (1972).

6. K. Bernauer and S. Fallab, Helv. Chim. Acta, 45, 2487 (1962).

7. K. Bernauer and S. Fallab, Helv. Chim. Acta, 44, 1287 (1961).

8. H. Siegel, P. Waldmeir, and B. Prijs, Inorg. Chem. Letters, 7, 161 (1971).

9. W. West and S. Pearce, J. Phys. Chem., 69, 1894 (1965).

10. E. Rabinowitch and L. Epstein, J. Amer. Chem. Soc., 63, 69 (1941).

11. A. R. Monahan and D. F. Blossey, J. Phys. Chem., 74, 4014 (1970)

12. A. R. Monahan, N. J. Germano and D. F. Blossey, J. Phys. Chem., 75, 1227 (1971).

13. K. Sauer, J. R. Lindsay Smith and A. J. Shultz, J. Amer. Chem. Soc., 88, 2681 (1966).

14. C. Chylewski, Angew. Chem. Internat. Edit., 10, 195 (1971).

15. W. West and B. H. Carroll, J. Chem. Phys., 19, 417 (1951).

16. A. R. Monahan, J. A. Brado and A. F. Deluca, J. Phys. Chem., 76, 1994 (1972).

17. A. B. P. Lever, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 7, H. J. Emeleus and A. G. Sharpe, Ed., Academic Press, New York, N. Y., 1965, p 27, and references therein.

18. L. D. Rollmann and R. T. Iwamoto, J. Amer. Chem. Soc., 90, 1455 (1968).

19. S. E. Sheppard and A. L. Geddes, J. Amer. Chem. Soc., 66, 1995 (1944).

20. J. G. Jones and M. V. Twigg, Inorg. Chem., 8, 2120 (1969).

21. M. Whalley, J. Amer. Chem. Soc., 866 (1961).

22. J. S. Anderson, E. F. Bradbrook, A. H. Cook and R. P. Linstead, J. Chem. Soc., 1151 (1938).

23. A. R. Monahan, J. A. Brado and A. F. Deluca, J. Phys. Chem., 76, No. 3, 446 (1972).

24. J. G. Jones, M. V. Twigg, Inorg. Nucl. Chem. Letters, 8, 305 (1972).

25. R. R. Das, R. F. Pasternack and R. A. Plane, J. Amer. Chem. Soc., 92, 3312 (1970).

26. L. C. Gruen, Aust. J. Chem., 25, 1661 (1972).

27. J. H. Weber and D. H. Busch, Inorg. Chem., 4, 469 (1965).

28. H. Kuhn, E. Schnaubel and H. Nother, in "Recent Progress in the Chemistry of Natural and Synthetic Coloring Matter and Related Fields," T. S. Gore, Ed., Academic Press, New York, N. Y., pp 561-572 (1962).

29. Physical Chemistry, third edition, F. Daniels and R. A. Alberty, Ed., John Wiley & Sons Inc., New York, N. Y., 250 (1967).

30. R. J. Blagrove and L. C. Gruen, Aust. J. Chem., 26, 225 (1973).