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Kinetic & Spectral Studies of Copper(II)-4,4',4'',4'''-Tetrasulfophthalocyanine in Aqueous Solution

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Stephen Wayne

1983

KINETIC AND SPECTRAL STUDIES OF COPPER(II)-4,4',4",4'"-TETRASULFOPHTHALOCYANINE IN AQUEOUS SOLUTION

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 Wayne Scholl
May 1983

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KINETIC AND SPECTRAL STUDIES OF COPPER(II)-4,4',4",4'"-TETRASULFOPHTHALOCYANINE IN AQUEOUS SOLUTION

Recommended March 21, 1983
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KINETIC AND SPECTRAL STUDIES OF COPPER(II)-4,4',4",4'"-TETRASULFOPHTHALOCYANINE IN AQUEOUS SOLUTION

Stephen W. Scholl   May 1983   36 pages
Directed by: Dr. R. D. Farina, Dr. L. J. Boucher, and
Dr. D. R. Hartman
Department of Chemistry   Western Kentucky University

The monomer-dimer equilibrium of CuTSPC^{4-} was examined by spectral methods in aqueous solution over a total dye concentration of 2×10^{-8}M to 8×10^{-7}M at 24°C. The value obtained for the dimerization constant, K_D, was $1.1 \times 10^{7}\text{M}^{-1}$ which is smaller than literature values. However, the discrepancy is not appreciable considering the differences in the methods used and the experimental conditions of the different solutions. Spectral measurements of the dimerization constant were made at only one temperature since the spectral changes were quite small when the temperature was varied. This observation is consistent with the small heat of reaction associated with the dimerization process which has been reported in the literature for this system. A comparison of the dimerization constant of CuTSPC^{4-} with other cations shows the following trend:

$$Cu^{2+} \geq Ni^{2+} > H^{+} > Zn^{2+} \sim VO^{2+} > Fe^{3+} > Co^{2+}$$

The larger dimerization constants of CuTSPC^{4-} and NiTSPC^{4-}

compared to the other tetrasulfonated phthalocyanines is attributed to the lack of axial ligand binding to these metals which enhances the dimerization process. Ligand binding studies made here and elsewhere on the $CuTSPC^{4-}$ and $NiTSPC^{4-}$ systems showed no evidence of ligand binding unlike the $FeTSPC^{3-}$ and $CoTSPC^{4-}$ systems where various ligands have been found to bind at the axial positions of these metals.

Kinetic measurements on the monomer-dimer equilibrium of $CuTSPC^{4-}$ in aqueous solution were made on the stopped-flow apparatus at 24°C using a total dye concentration range of 1×10^{-6}M to 1×10^{-5}M. The rate constants for the formation and dissociation of the $CuTSPC^{4-}$ dimer are $3.24 \times 10^{6} M^{-1} s^{-1}$ and $0.27\ s^{-1}$, respectively. Activation parameters could not be obtained due to the small spectral changes which occur at different temperatures and hence cannot be measured on the stopped-flow apparatus. The kinetic data show that the formation and dissociation rate constants of $CuTSPC^{4-}$ in aqueous solution is similar to those of $NiTSPC^{4-}$ and $VOTSPC^{4-}$ systems. All these tetrasulfonated metallophthalocyanine systems show no evidence of ligand binding to the central metal ion and have similar dimerization constants. On the other hand the lower dimerization constant of $CoTSPC^{4-}$ relative to these systems can be attributed to the smaller rate constant associated with the formation of the dimer. The presence of axial ligands on the central metal ion is believed to inhibit the formation of the dimer in $CoTSPC^{4-}$.

I. INTRODUCTION

Phthalocyanines are macrocyclic compounds which are of industrial and biological importance. Industrial interest has been demonstrated by the many studies made on the semiconductivity, photoconductivity, photochemical reactivity, photosynthetic activity, luminescence and fluorescence properties associated with the highly conjugated system of phthalocyanine and metallophthalocyanines.(1) Furthermore, their staining properties are of interest to the dye industry.(2) One of the main reasons for the biological interest lies in the porphyrin-like structure of these compounds which makes them useful models for studying biological processes involving hemoproteins.(3)

The phthalocyanine ring system consists of four isoindole units linked by azo nitrogens and is highly aromatic having 18 pi electrons which conforms to Huckels $4n+2$ rule. These compounds are amphoteric in that hydrogens can be lost from two of the four nitrogen donor atoms to form the dianion or protonation can occur at the other two nitrogen donor atoms. The structure of a typical metallophthalocyanine is shown in Figure 1.

A. Polymerization of Metallophthalocyanines

The spectral characteristics of tetrasulfophthalocyanine, ($TSPC^{4-}$), and its various transition metal derivatives, ($MTSPC^{n-}$), have been studied in water as well as in various

TYPICAL STRUCTURE OF A TETRASULFONATED METALLOPHTHALOCYANINE COMPLEX

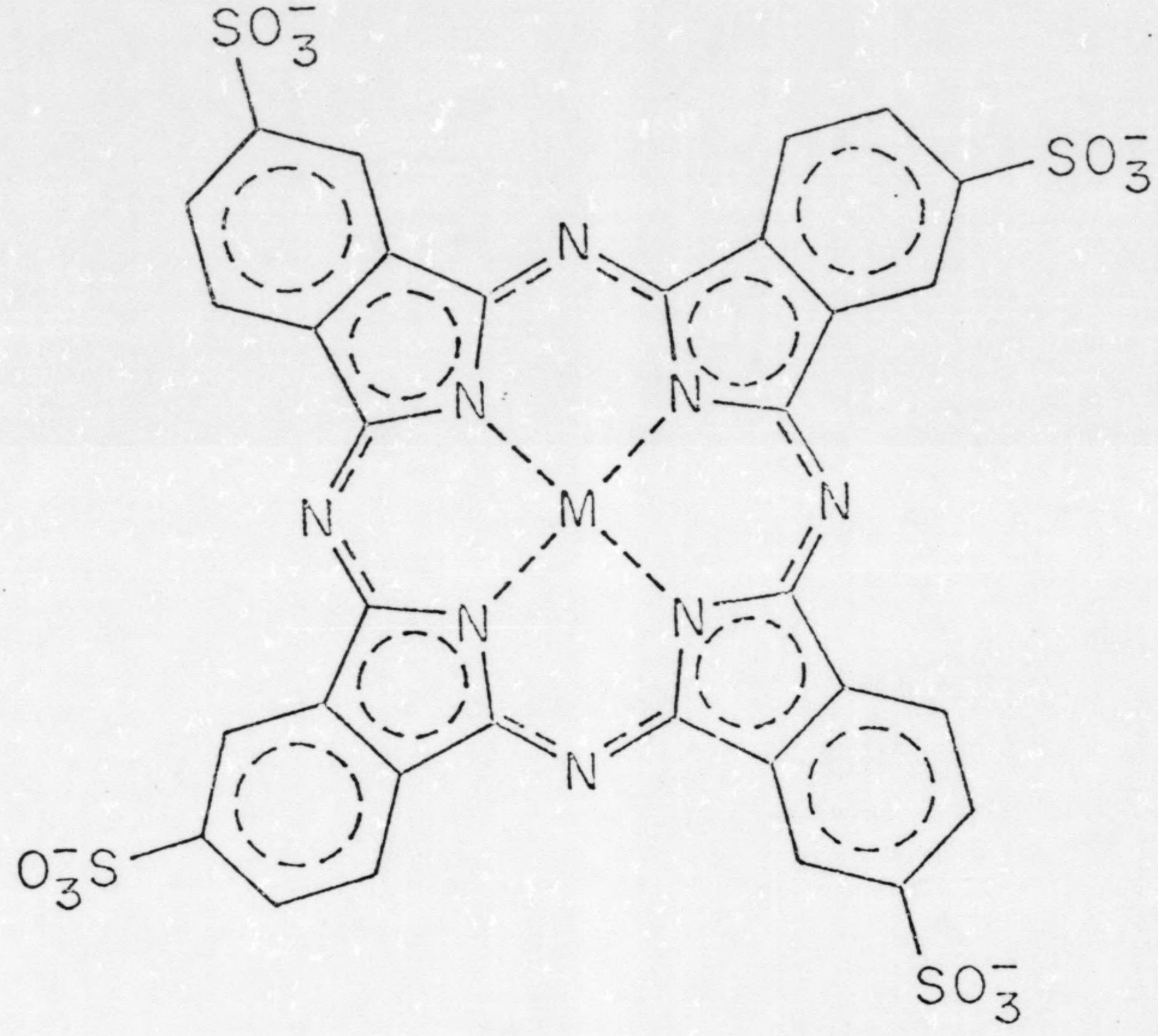


FIGURE 1

other solvents.(2,4-16,22) In aqueous solution these compounds do not follow Beers Law for their visible absorbance,and this behavior has been attributed to aggregation of the dye.(10,18) The visible spectra of these complexes in dilute solution, ($<10^{-5}$M), contain two primary bands in the 600-700 nm region which have been interpreted in terms of a monomer-dimer equilibrium.(4,6,7,13) The first band at the longer wavelength has been assigned to the monomer species while the shorter wavelength band has been attributed to the dimer species. Another feature of the spectra is the formation of an isosbestic point with various dye concentrations using optical cells of appropriate path length. The presence of an isosbestic point at dilute concentrations, (10^{-7}-10^{-5}M), has been ascribed to a monomer-dimer equilibrium. High concentrations favor formation of the dimer while low concentrations favor the monomeric species. Thus, when these solutions are diluted, the dimer dissociates into two monomer units. Spectral studies support these arguments in that diluting solutions of phthalocyanines and/or their metal derivatives reveal an increase in intensity of the band at the longer wavelength (monomer) while there is a corresponding decrease in intensity of the band at the lower wavelength (dimer). Similar behavior has been exhibited by other compounds, such as porphyrins, which aggregate in solution.(9-12,14,18-22)

The equilibrium between monomer and dimer of $MTSPC^{n-}$ systems has been shown to be influenced by conditions such as temperature, ionic strength, and the dielectric constant of the solvent. Repulsive interactions between negatively charged sulphonate groups on the TSPC^{4-} ring is one of the factors influencing aggregation. Repulsion inhibits aggregation and any factors that reduce this effect will promote aggregation. High solvent dielectric constant and high ionic strength are two conditions that will reduce repulsion between negatively charged monomer units. The effect of solvent dielectric constant has been shown by the addition of organic solvents such as ethanol, acetone, DMSO and methanol which have lower dielectric constants than water and hence promote disaggregation.(8,9,13,14) Futhermore, the addition of urea to aqueous solutions increases the dielectric constant of the solution which would tend to shift the equilibrium to the dimer. However, the addition of urea to aqueous CuTSPC^{4-} solutions has resulted in a slight monomeric shift.(13) This has been attributed to the breaking down of the water structure surrounding the dye by urea thus reducing the exclusion of the dye and allowing some dimer dissociation. Strong solvent interactions exclude dye molecules from solution and favor aggregation.(15) The net effect of these two opposing forces on the CoTSPC^{4-} system is a slight shift of the equilibrium to the monomer species as stated above. The ionic strength of the dye solution has an effect on the monomer-dimer equilibrium in that ion pairing can occur between the sulphonate groups on the TSPC^{4-} ring and the cations of salts added to the solution. This would tend to reduce the electrostatic charge associated with the MTSPC^{n-} monomer units and in turn lower the repulsion between these dye species and promote aggregation. Many studies have shown that the addition of salts to $MTSPC^{n-}$ solutions causes a shift in the equilibrium to the dimer.(13,14,17,22) Similar salt effects have been observed in porphyrin systems.(24,25) Temperature studies on $MTSPC^{n-}$ systems show that the equilibrium is shifted to the monomer with an increase in temperature.(9,13,14,16,22)

The dimerization of $CuTSPC^{4-}$ in aqueous solution has previously been studied by Gruen et al.(12) In their study, however, the monomer absorptivity coefficient, (ε_m) was determined in nonaqueous solvents and the concentration quotients not corrected for varying ionic strength. For these reasons a redetermination of the dimerization constant was made in this study, where the ε_m value was obtained in deionized water and the effect of ionic strength on the dimerization constant was considered.

B. Kinetic Study

A review of the literature does not reveal very many kinetic studies involving the dimerization of $MTSPC^{n-}$ systems.(9,10,16,22,23) In most of these studies, the stopped-flow apparatus was utilized together with the concentration-jump relaxation technique. In all but one system,(16) aqueous solutions were used where appreciable amounts of both monomer and dimer were present. All of these measurements were made under natural ionic strength conditions with no salts added in order to limit the aggregation to the dimer stage only. Moreover, ambient temperatures and higher were used as well as low dye concentrations to further ensure that no polymerization beyond the dimer would occur. There have been no kinetic studies reported on the dimerization of $CuTSPC^{4-}$, and for this reason a kinetic study incorporating experimental conditions described above was made on this sytem.

C. Ligand Binding Studies

Transition metal ions usually have a definite coordination number in solution. Their geometries are determined by a number of factors associated not only with the transition metal but also the type of ligands available for coordination. The metal ion in the $MTSPC^{n-}$ complex is coordinated to four positions of the $TSPC^{4-}$ ring. However, many transition metals have coordination numbers which are greater than four allowing water molecules or other ligands in solution to bind at the axial positions of the $MTSPC^{n-}$ complexes. Ligand binding studies of these axial positions have been conducted, especially in the $FeTSPC^{3-}$ system, and the kinetics reported in the literature.(3,16,26-39) Molecular oxygen is one ligand that has been extensively studied with various phthalocyanine complexes.(39-49)

In the present work, binding studies were conducted with $CuTSPC^{4-}$ using a number of different ligands. Also, an attempt was made to examine the effect of O_2 and CO_2 binding to this complex.

II. EXPERIMENTAL

This section describes the materials, apparatus, sample handling, spectral measurements and preliminary experiments involved in this project.

A. Materials

1. $CuTSPC^{4-}$

The tetrasodium salt of $CuTSPC^{4-}$ used in this study was obtained from Eastman Kodak Co. The compound was additionally purified according to the method described by Weber and Busch.(50) The absorbance of this compound in DMSO and DMF was low compared to reported values(51) and bands of the free ligand were present. Therefore, $CuCl_2$ was added in the purification procedure to complex any free $TSPC^{4-}$.

2. Chemicals

The following chemicals were used without further purification:

Chemical	Company	Grade
Pyridine	Baker	Reagent
Ethanol	U.S. Industrial Co.	Anhydrous
DMF	M.C.B.	Spectral
DMSO	M.C.B.	Reagent
Copper Chloride	M.C.B.	Reagent
Sodium Cyanide	Baker	Reagent
Potassium Cyanate	M.C.B.	Reagent
Sodium Perchlorate	G.F.S. Chem. Co.	Reagent
Sodium Sulfide	Fisher	Reagent
Sodium Thiocyanate	Baker	Reagent
Urea	Mallinkrodt	U.S.P.
Sodium Azide	Baker	Reagent

B. Apparatus

1. Cary Model 14 Recording Spectrophotometer

All spectral measurements were made with a Cary Model 14 recording spectrophotometer which can be used in the ultraviolet, visible, and near infrared spectral regions. In this study, spectral measurements were made over a wavelength range of 300 nm to 720 nm.

During the spectral measurements, the temperature of the solutions in the optical cells was maintained by using an optical cell sample jacket, Cary # 1444100 which can be inserted into the sample compartment of the Cary Model 14. A Haake Model FE constant temperature circulator bath was used to circulate the water through the sample jacket. This assembly allows the temperature of the solution in the spectral cells to be maintained within ± 0.03°C over a temperature range of 25°C to 80°C. In order to achieve lower temperatures, ice water from a water bucket was fed to the Haake circulator by a vertical centrifugal immersion pump, Model 26159, manufactured by Gelbar Pump Company.

2. Portable Microprobe Thermometer

The temperature of the dye solutions was accurately measured with a portable microprobe thermometer, Model Bat-4, manufactured by Bailey Instrument Company, Inc. The liquid immersion probe, Model # 8506-75, is 0.025 inches in diameter, three feet in length and is completely encased in a thin, flexible teflon sheath.

3. pH Meter

The pH measurements on the dye solutions were made with a Sargent-Welch Model IP pH meter. The meter was calibrated at 25°C with pH 4.0 and 7.0 buffer solutions, also from Sargent-Welch. A new Orion gel-filled combination electrode, catalog # 910500,was used with the pH meter.

4. Analytical Balance

All weighings were made on a Sartorius analytical balance which weighs to within ± 0.1 mg. The dye concentrations were determined from both spectroscopic and weight measurements. The results from each method were in excellent agreement.

5. Stopped-Flow Apparatus

A glass-teflon spectral stopped-flow apparatus was used to measure the monomer-dimer equilibrium kinetics since this process is rapid. The stopped-flow apparatus consists of two 50 ml. glass syringes mounted on an aluminum pushing block and surrounded by glass jackets to allow liquid from a constant temperature bath to circulate around them for temperature control. The syringe is attached to a three-way stopcock connected to an Atom-Mech 8-jet, 2mm teflon mixing chamber. The mixing chamber is held firmly in a brass, constant temperature control block cemented to a bakelite jacket with hose attachments to allow liquid from a constant temperature bath to circulate for temperature control. Reagents are kept in glass reservoirs with plexiglass jackets for temperature control. These reagents can be drawn into the syringes via three-way stopcocks.

The flow of each reactant from the syringes is split into two streams before combining into the 8-jet mixing chamber. The effluent stream from the mixing chamber passes through a quartz observation tube (2mm light path) which is attached to the mixing chamber and held firmly in a channel formed between two aluminum blocks. Light from an Aminco # 4-8459 grating monochrometer traverses the short length of the quartz observation tube (tube diameter) with the width of the light beam controlled by means of an adjustable slit in the monochrometer. The transmitted light beam is detected and amplified by a Varian EMI # 6254B photomultiplier tube. The output from the photomultiplier tube is connected to a microammeter to measure the photomultiplier current which is maintained to within 9-10 microamps on each kinetic run. The current from the microammeter is directed to an Aminco # 4-8418A Kinetic Photometer for optimization of the dynamic photometric signal, i.e., best signal to noise ratio for the electronics involved. The output from the kinetic photometer is fed to a Type 3A9 Differential Amplifier of a Tektronic Type R 564B Mod 08 Storage Oscilloscope where the photomultiplier current is converted to voltage. The time rate of change in the signal voltage during the course of a reaction is monitored with a Tektronix 3B3 Time Base Unit which controls the sweep rate of the signal across the screen of the oscilloscope.

The stream which passes the observation tube is fed to one arm of a three-way stopcock. The second arm is connected to a vertical-mounted 50 ml stopping syringe while the remaining arm is used for sampling and disposal of the mixed solutions.

By suitable positions of the 3-way stopcock, the reactant solutions can be withdrawn into the two reactant syringes and then after being thoroughly mixed in the mixing chamber can be pushed through the observation tube manually. When the plunger from the stopping syringe strikes the mechanical microswitch mounted on the stopping block located beneath it, the flow instantly stops while triggering the oscilliscope which is electrically connected to the microswitch.

The course of the reaction can be followed on the screen of the scope where the transmittance of the stationary solution is recorded in voltage as a function of time. The apparatus is designed to measure reactions with half-times as fast as 3 milliseconds. An Aminco 120 watt Tungsten Iodide lamp is the light source in the visible region of the light spectrum while a PEK X-76 Xenon Lamp is the light source in the ultraviolet region. Power supplies for the photomultiplier tube and light sources were Power Design Model 1565 High Voltage DC Power Supply and a Harrison LVR Model 6274A, respectively. The screen of the oscilliscope was photographed with a Tektronix Polaroid C-12-R camera loaded with Polaroid Type 47 black and white film. A schematic diagram of the stopped-flow apparatus is shown in Figure 2.

C. Spectroscopic Measurements

1. Sample Handling

All spectral measurements in this study were made on aqueous solutions of $CuTSPC^{4-}$ at natural ionic strength except where otherwise noted. The solutions were prepared by diluting a 10^{4-}M stock solution of $CuTSPC^{4-}$. The dye

SCHEMATIC DIAGRAM OF THE STOPPED-FLOW APPARATUS

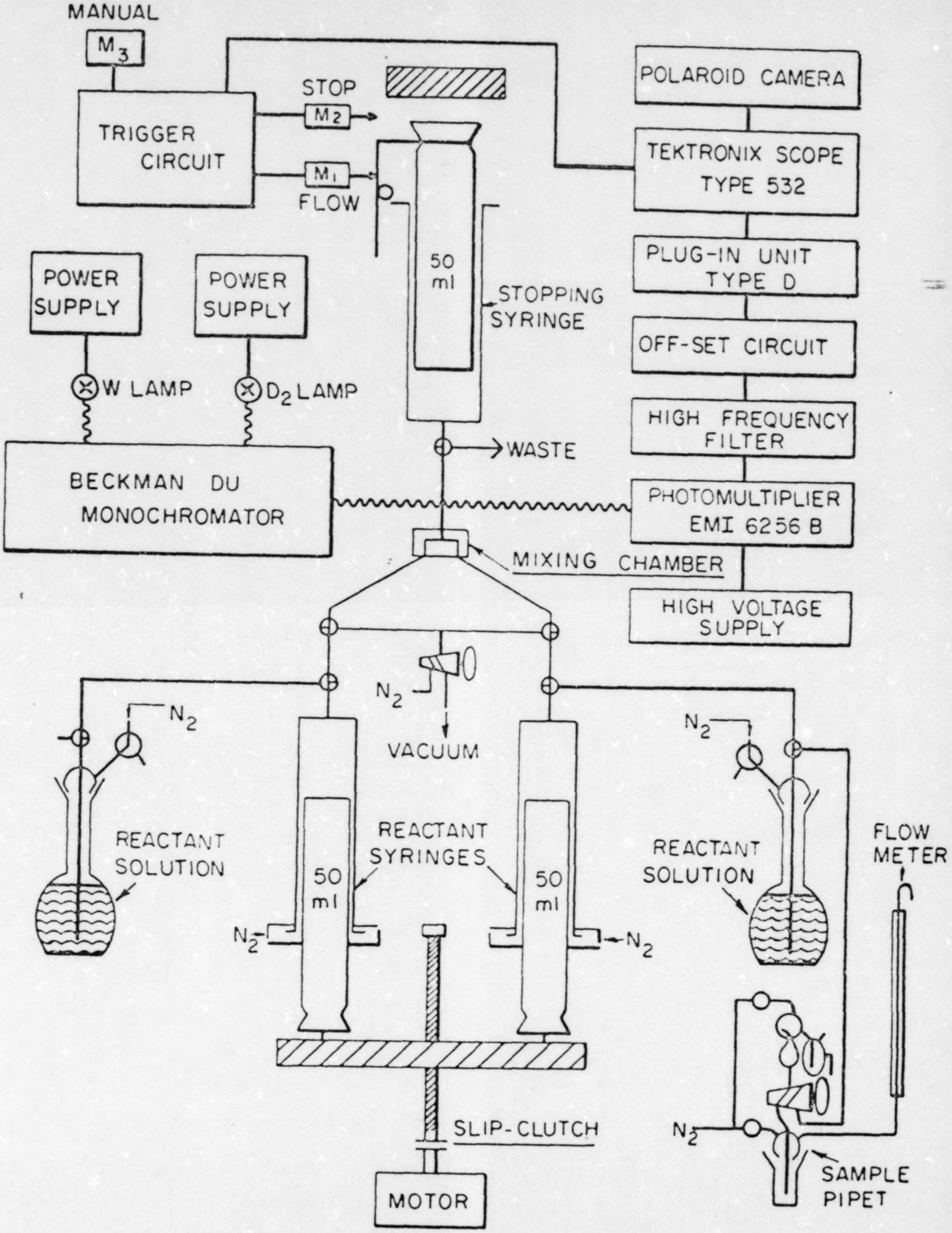


FIGURE 2

concentrations used in each study are listed in the sections describing those studies. All solutions were used within 24 hours of preparation although it was found that the spectra for these solutions did not change significantly after aging 2-4 days.

Spectral measurements of the solutions were made in cylindrical spectral cells of varying path lengths. The path length of cells used were .1 cm, .5 cm, 1 cm and 10 cm. The cell path length was selected to maintain the absorbance in a measurable range, 0-2 absorbance units.

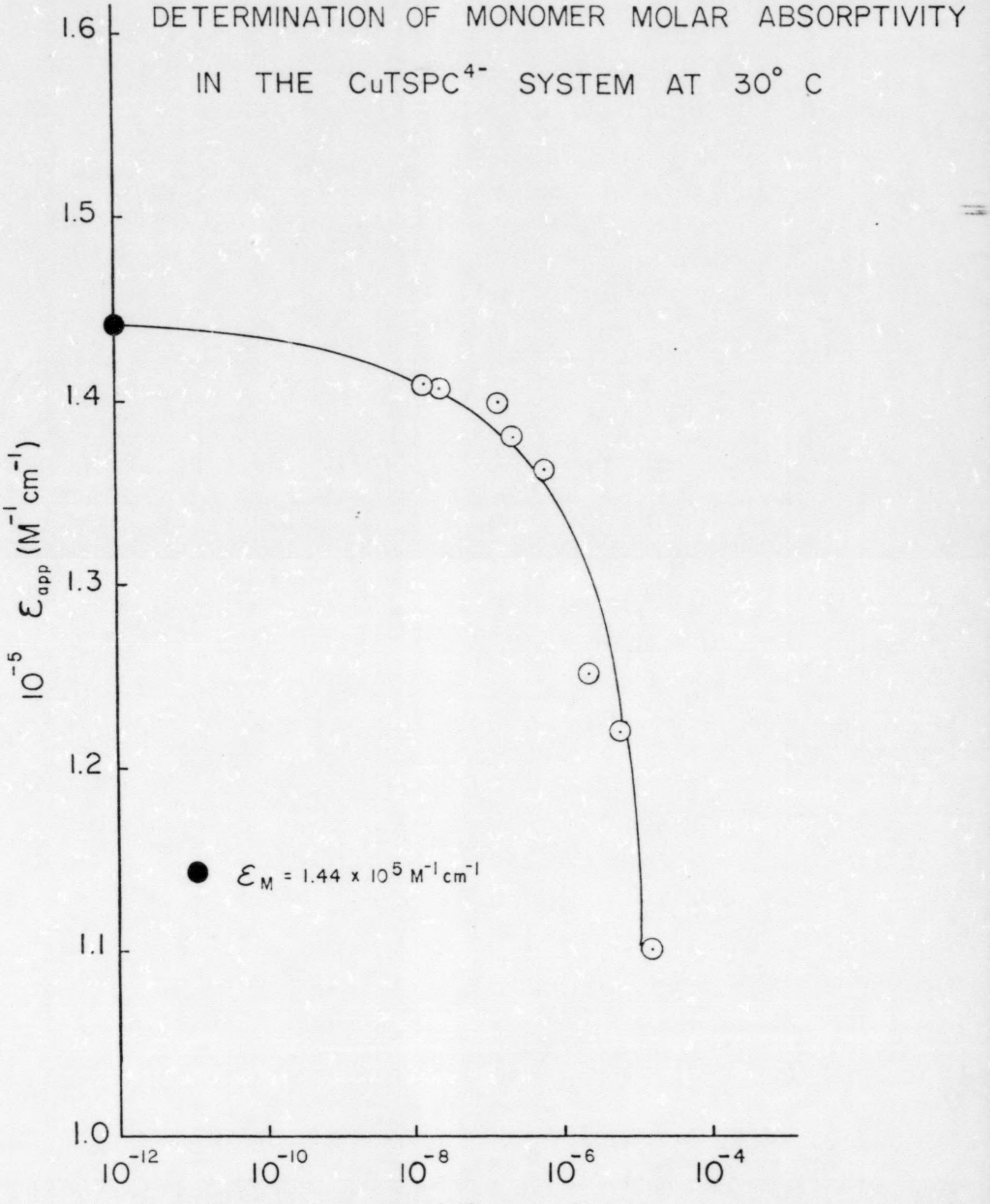
D. Determination of Monomer Absorptivity Coefficient

Spectral measurements for the monomer absorptivity coefficient, (ε_m), were made at 30°C in the visible range using dye concentrations of $4x.0^{-5}$ - $4x10^{-9}$ M. Although temperature effects on the equilibrium were found to be slight, the highest possible temperature was used to minimize the formation of the dimer. The temperature selected was 30°C because it was found that at temperatures greater than this the absorbance of the solutions began to decrease. This suggested dissociation of the complex or adsorption of the dye to the spectral cell walls rather than a shift in the equilibrium so temperatures above 30°C were not used. The spectra obtained for the aqueous system was typical of metallophthalocyanines and compared well with previously reported $CuTSPC^{4-}$ spectra.(9,17,24,53) The spectra contained an isobestic point at 644 nm which is indicative of the monomer-dimer equilibrium. Also, the spectra contained the large peak at 670 nm (monomer) and the smaller peak at 630 nm (dimer) as well as other features of the $CuTSPC^{4-}$ spectra.

The monomer absorptivity coefficient was determined graphically. Apparent absorptivities, $\varepsilon_{app} = A_{670}/C_T$),were determined by measuring the absorbance at 670 nm (A_{670}) for each dye concentration (C_T) over the range stated above. A plot of ε_{app} versus C_T was constructed and ε_{app} extrapolated to infinite dilution where, theoretically, the dye is completely monomeric and $\varepsilon_{app} = \varepsilon_m$ (see Figure 3). The value obtained for ε_m at 30°C for aqueous $CuTSPC^{4-}$ is $1.44 \times 10^5\ M^{-1}cm^{-1}$. This value is in good agreement with the result obtained in 50% urea solution where the dye is reported to be completely monomer. That value is $1.425 \times 10^5\ M^{-1}cm^{-1}$.

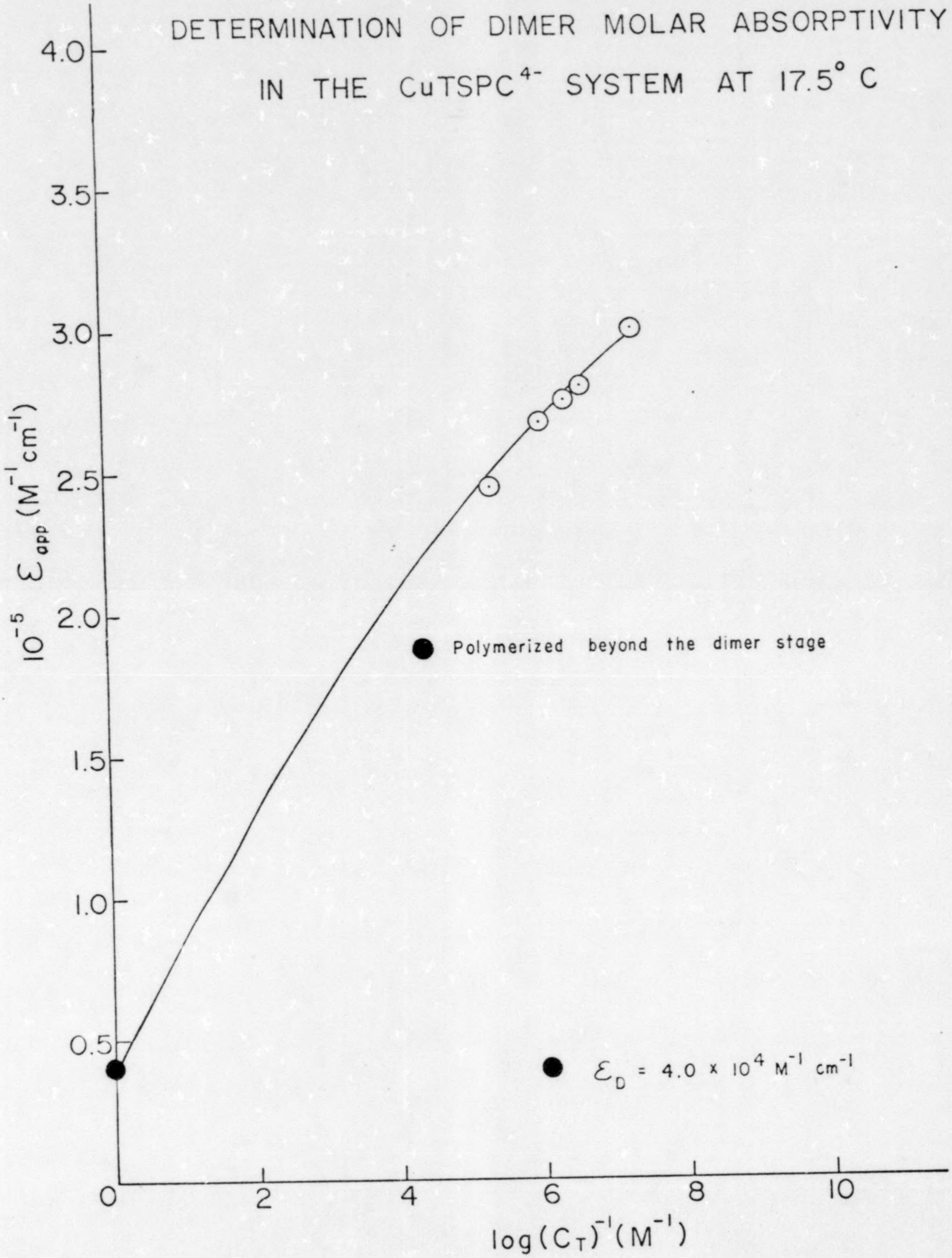
E. Determination of Dimer Absorptivity Coefficient

A similar spectral study was conducted at 17.5°C to determine the dimer absorptivity coefficient (ε_D). Measurements were made on dye concentrations ranging from 4×10^{-7} - $4 \times 10^{-6}M$. The temperature and concentrations were chosen to favor the dimer as much as possible. Dye concentrations greater than $10^{-5}M$ were not used because the dye reportedly forms higher aggregates at this concentration and above.(4) The apparent absorptivity was calculated for each dye concentration as before where $\varepsilon_{app} = 2A_{670}/C_T$ and a plot of ε_{app} versus log ($1/C_T$) was made (see Figure 4). This plot was extrapolated to infinite concentration where, theoretically, the dye is fully dimerized and $\varepsilon_{app} = \varepsilon_D$. The value of ε_D at 670 nm for aqueous $CuTSPC^{4-}$ was found to be $4.0 \times 10^4 M^{-1}cm^{-1}$, which is in close agreement with the literature value(4).



DETERMINATION OF MONOMER MOLAR ABSORPTIVITY IN THE CuTSPC^{4-} SYSTEM AT 30° C

FIGURE 3



DETERMINATION OF DIMER MOLAR ABSORPTIVITY IN THE $CuTSPC^{4-}$ SYSTEM AT 17.5° C

FIGURE 4

F. Equilibrium Study

Methods for determining the dimerization constant of metallophthalocyanines are reported in the literature.(8) A detailed description of the treatment of the equilibrium data is presented in the Results and Discussion section of this thesis.

The equilibrium measurements were conducted at 24°C with aqueous dye samples over the concentration range of $8 \times 10^{-7} - 2 \times 10^{-8}$M under natural ionic strengths. The spectra of these solutions showed that with dilution the spectral band positions remained the same but the relative intensities of the monomer and dimer bands varied as previously reported (see Figure 5).

The effect of temperature on the equilibrium was also studied as previously mentioned. There was a slight shift to monomer with temperature increase using the temperatures of 17.5°C, 24°C and 30°C. At temperatures much above 30°C the monomer band began to decrease.

G. Kinetic Studies

The formation and dissociation rates of the $CuTSPC^{4-}$ dimer are rapid processes which can be followed on the stopped-flow apparatus as were the reactions of other metallophthalocyanines complexes.(5,8,9,10) The specific method involves perturbing the monomer-dimer equilibrium of $CuTSPC^{4-}$ in aqueous solution using the concentration jump method described in the literature.(11) The equilibrium of the $CuTSPC^{4-}$ system favors the dimeric species but with dilution

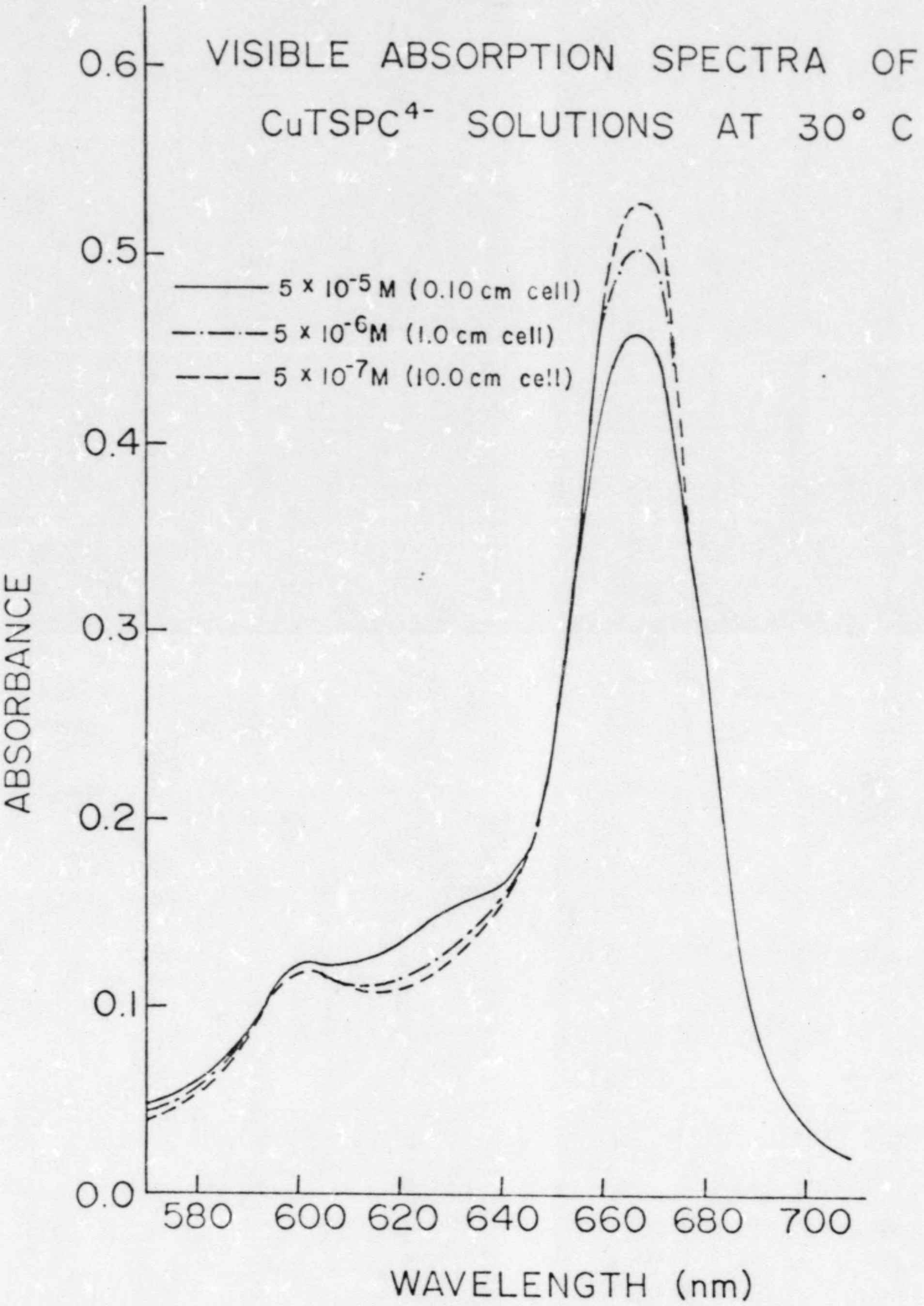

VISIBLE ABSORPTION SPECTRA OF
CuTSPC^{4-} SOLUTIONS AT 30° C
5×10^{-5} M (0.10 cm cell)
5×10^{-6} M (1.0 cm cell)
5×10^{-7} M (10.0 cm cell)
ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
580
600
620
640
660
680
700
WAVELENGTH (nm)

FIGURE 5

a shift to the monomeric species occurs. Therefore, dye solutions where the total concentration of $CuTSPC^{4-}$ varied from $1 \times 10^{-6} - 1 \times 10^{-5}M$ were rapidly mixed with equal amounts of water on the stopped-flow apparatus where the shift to monomer was monitored by following the increase in absorbance at 670 nm. This shift was monitored from the moment of perturbation until a new equilibrium is reached. The re-equilibration step is a first order process and follows the relationship

$$d\Delta C_m/dt = 1/\tau \Delta C_m$$

where ΔC_m = the difference in monomer concentration between time t and infinite time where a new equilibrium is reached,

τ = relaxation time for the re-equilibration process.

The relaxation times were obtained from the slopes of plots involving ln ΔC_m versus time for each dye solution. All plots were linear indicative of a first order process. Plots of τ^{-2} versus C_T allow the formation and dissociation rate constants of the $CuTSPC^{4-}$ dimer to be determined (see Results and Discussion section). All stopped-flow experiments were performed at 24°C where appreciable amounts of monomer and dimer are present. Fresh solutions were prepared for each run and all runs were performed in at least duplicate.

H. Preliminary Experiments

1. Ligand Binding Studies

The addition of ligands to aqueous solutions of $CuTSPC^{4-}$ was studied spectrally. The ligands tested were pyridine, thiocyanate, cyanide, cyanate, sulfide and azide. There was no significant change in the spectrum of the $CuTSPC^{4-}$ solutions in the presence of these ligands. These results are consistent with those of Busch et al.(1)

2. Effect of Dissolved Gases on the Monomer-Dimer Equilibrium

In this study the effect of dissolved gases on the monomer-dimer equilibrium of $CuTSPC^{4-}$ was studied. The gases of interest in this study were O_2 and CO_2. The effects of these gases were tested before and after purging the dye solutions with nitrogen by taking pH and spectral measurements. The dye solutions ranged in concentration from 4×10^{-6} M to 4×10^{-8} M. The runs were performed at a temperature of 24°C. The solutions were deoxygenated either in a 50 ml side arm flask by running the nitrogen gas through a fritted gas dispenser or in a 6-inch side arm test tube by bubbling through a Pasteur pipette. The deoxygenated solutions were transferred to the spectral cells and capped. Absorbance readings were made immediately.

The deaerating effect was further studied by measuring pH changes that would result from removing CO_2 from the solutions. The pH of solutions of dye concentrations of 4×10^{-6} M, 4×10^{-7} M and 4×10^{-8} M as well as deionized water was measured before and after deaeration. After deaerating a solution, the pH reading was made by placing the pH electrode directly into the side arm vessel used in the deaeration step.

III. RESULTS AND DISCUSSION

This section is divided into three parts. The first part deals with the spectral study of the dimerization of $CuTSPC^{4-}$ in aqueous solution while the other parts examine the ligand binding properties and kinetics of dimerization associated with the complex.

A. Dimerization of $CuTSPC^{4-}$

The spectra of aqueous solutions of $CuTSPC^{4-}$ show an isosbestic point at 644 nm for solutions in the concentration range of $4 \times 10^{-6} - 4 \times 10^{-9}$M which is indicative of a monomer-dimer equilibrium reported in the literature for this complex and other $MTSPC^{n-}$ systems.(2,5,9,10,13,14,17,22,55,58) Assuming an equilibrium exists between monomer (M) and dimer (D), the dimerization constant, K_D, can be determined from spectral measurements using the following equations:

$$2M = D \qquad (1)$$

$$C_T = \bar{C}_M + 2\bar{C}_D \qquad (2)$$

$$A/L = \varepsilon_M\bar{C}_M + \varepsilon_D\bar{C}_D \qquad (3)$$

$$K_D = \bar{C}_D\gamma_D/(\bar{D}_M\gamma_M)^2 \qquad (4)$$

where C_T, $\bar{C}_D$, and $\bar{C}_M$ represent the concentrations of the total dye and equilibrium concentrations of dimer and monomer, respectively in eq. (2). In eq. (3), A is the absorbance of the solution at a given wavelength, L is the optical path length, and ε_M and ε_D are the optical absorptivities of monomer and dimer, respectively. The parameters γ_D and γ_M in eq. (4) are the respective activity coefficients. At infinitely dilute concentrations, these activity coefficients are unity simplifying eq. (4) to eq. (5):

$$K_D = \bar{C}_C/\bar{C}_M^{\,2} \qquad (5)$$

where $\lim_{C_T \to 0}, \gamma_D/\gamma_M^2 \to 1.0$.

In this work, $\bar{C}_D/\bar{C}_M^{\,2} = Q_D$, a concentration quotient. The values of ε_M and ε_D can be obtained experimentally as described earlier. The values of C_T are obtained for each solution from the weight measurements of the solid dye dissolved in a known volume of water while A/L was determined with the Cary Model 14 recording spectrophotometer. Therefore, the equilibrium amounts of monomer at different total dye concentrations can be determined by combining eqs. (2), (3) and (4) to yield

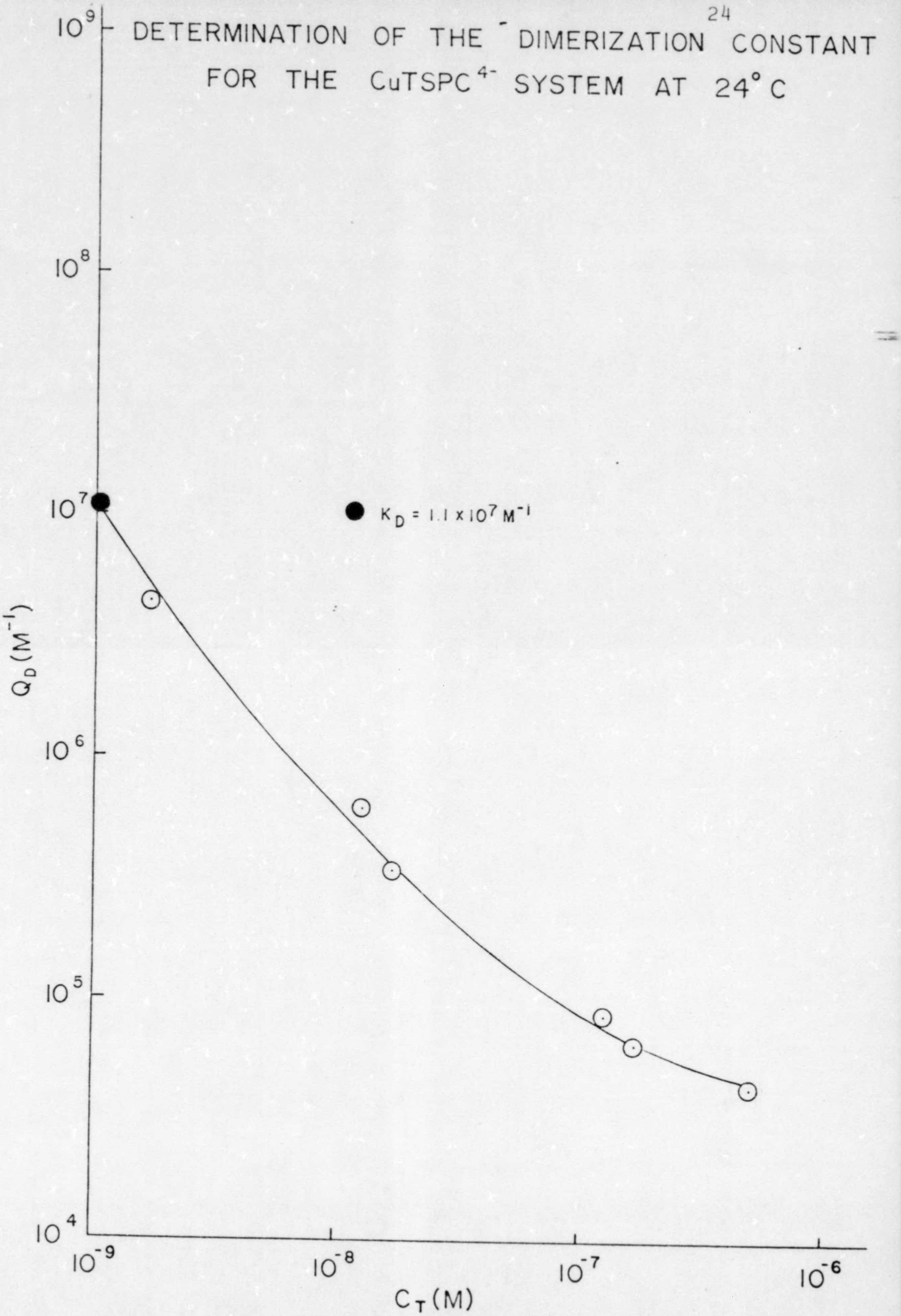
$$\bar{C}_M = (2A/L - \varepsilon_D C_T)/(2\varepsilon_M - \varepsilon_D) \qquad (6)$$

from which the dimer concentration is determined from eq. (2). A value of Q_D, the concentration quotient, can be obtained from eq. (5) at each total dye concentration. Table 1 contains the experimental data used in calculating Q_D at 24°C. Using the Q_D values at different total dye concentrations, K_D was determined graphically from a plot of Q_D versus C_T where at infinite dilution $K_D = Q_D$. The value of K_D obtained at 24°C is $1.1 \times 10^7\ M^{-1}$ (see Figure 6). The K_D determined here is smaller than that reported by Blagrove and Gruen(53) ($2.5 \times 10^7\ M^{-1}$). However, the discrepancy is not appreciable considering the differences in the methods used. For example, the value of ε_M determined in this work was obtained in water while the value used by the other workers was obtained in 20% ethanol. Secondly, no attempt was made to consider the effect of ionic strength on the dimerization constant. Consequently,

Table 1

Concentration Quotients of the $CuTSPC^{4-}$ Dimerization in Aqueous Solution at 24°C

C_T (M)	C_M (M)	C_D (M)	Q_D (M^{-1})
$8x10^{-7}$	$7.5x10^{-7}$	$2.5x10^{-8}$	$4.44x10^{4}$
$4x10^{-7}$	$3.8x10^{-7}$	$9.7x10^{-9}$	$6.7x10^{4}$
$2x10^{-7}$	$1.9x10^{-7}$	$3.2x10^{-9}$	$8.62x10^{4}$
$4x10^{-8}$	$3.9x10^{-8}$	$5.2x10^{-10}$	$3.45x10^{5}$
$2x10^{-8}$	$2.0x10^{-8}$	$2.4x10^{-10}$	$6.37x10^{5}$
$4x10^{-9}$	$3.9x10^{-9}$	$6.6x10^{-11}$	$4.41x10^{6}$



DETERMINATION OF THE DIMERIZATION CONSTANT FOR THE CuTSPC^{4-} SYSTEM AT 24° C

FIGURE 6

our value is reported at infinite dilution while the literature value was obtained at an averaged natural ionic strength. Similar arguments are applicable to the K_D value of 1.4×10^8 M^{-1} at 25°C reported in reference 5. On the other hand, a K_D value of 1.6×10^7 M^{-1} was reported at 61°C by Bernauer and Fallab(17) which is in excellent agreement with our result since temperature effects on the K_D value of $CuTSPC^{4-}$ are small.(51) This observation was confirmed in our studies where very minor changes in the visible spectra occurred over a temperature range of 17.5°C to 30°C. This indicates that ΔH for the dimerization is small and hence K_D varies slightly with temperature.

Table 2 lists the K_D values for several tetrasulfonated metallophthalocyanines including the uncomplexed ligand. The order of stability constants of the dimer is $Cu^{2+} \geq Ni^{2+} > H^+ > Zn^{2+} \sim VO^{2+} > Fe^{3+} > Co^{2+}$. One explanation for the greater stability of the Ni^{2+} and Cu^{2+} complexes compared to VO^{2+}, Fe^{3+} and Co^{2+} systems is the tendency of the VO^{2+}, Fe^{3+} and Co^{2+} complexes to undergo axial ligand binding. These metals have preferred cordination numbers greater than 4. Thus, the axial binding of H_2O molecules by these complexes in aqueous solution would inhibit dimer formation since these ligands would have to be removed for dimer formation to occur. The Cu^{2+} and Ni^{2+} complexes have preferred coordination numbers of 4 as evidenced by the observation that no axial binding by complexes of these metals has been found.(50) Additional factors must be involved in the Fe^{3+} and VO^{2+} complexes since the dimer stability is appreciably larger than that of the

Table 2

Dimerization Constants of Some MTSPC Complexes

T (°C)	Cation	log K_D* (M^{-1})
61	Cu^{2+}	7.2**
58	Ni^{2+}	7.1**
62	H^+	7.0
58	Zn^{2+}	6.0
60	VO^{2+}	6.0
60	Fe^{3+}	5.9
58	Co^{2+}	5.3**

*$K_D = C_D/C_M^2$

**Obtained at zero ionic strength while the others were reported at natural or low ionic strength.

Co^{2+} complex. One explanation for the greater stability of the $FeTSPC^{3-}$ dimer could be that the overall charge of the complex is -3 due to the metal center being +3 charge. This would reduce the electrostatic repulsion between the monomer species on approach and hence facilitate dimerization. In the case of the VO^{2+} complex, the possibility of an oxygen-bridged dimer would facilitate dimerization for this complex. Oxygen bridging has been shown to occur in electron transfer reactions involving the Vanadium complexes lending some support for this argument.(9)

B. Dimerization Kinetics of $CuTSPC^{4-}$

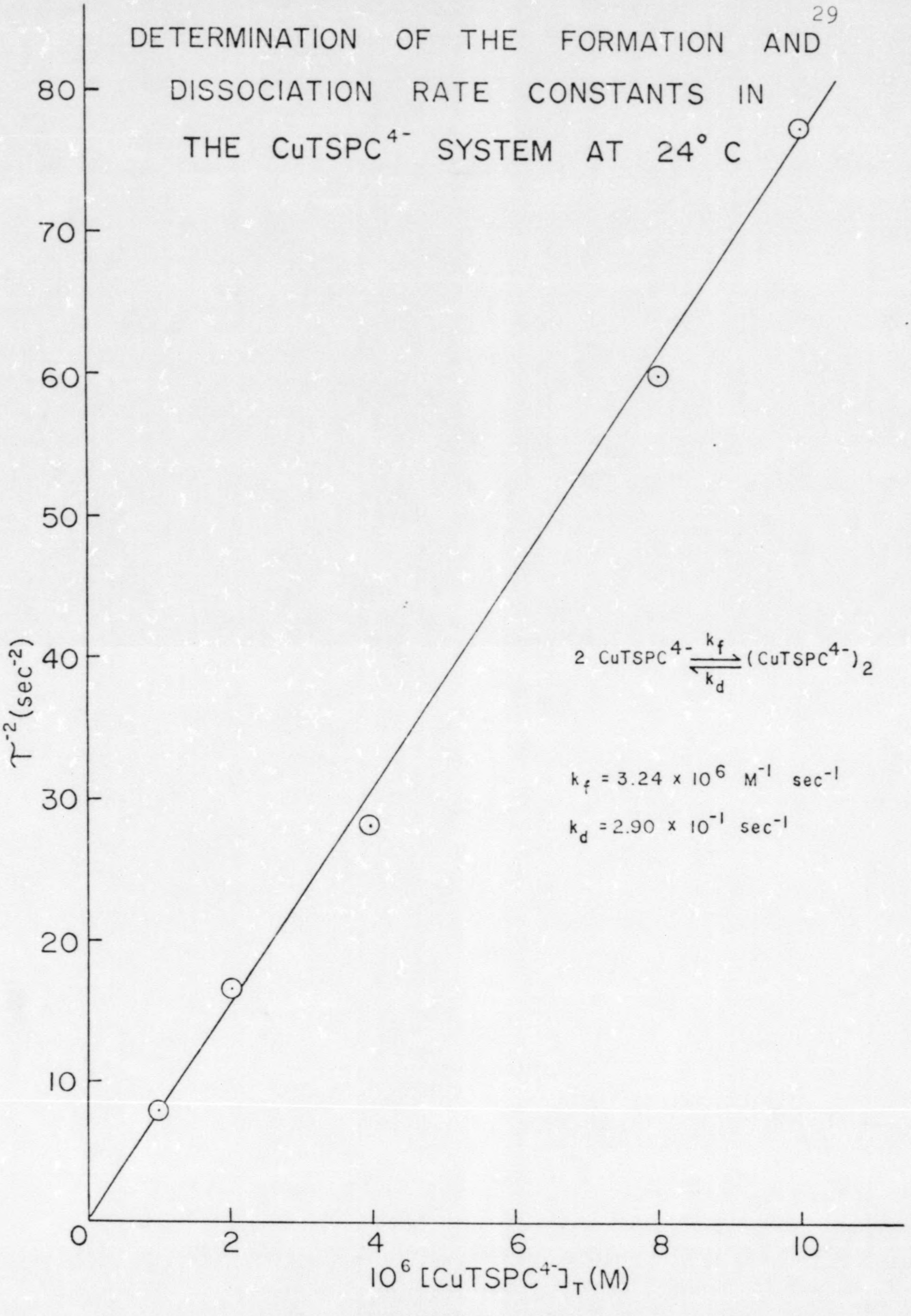
Kinetic measurements of the monomer-dimer equilibrium of $CuTSPC^{4-}$ in aqueous solution were made on the stopped-flow apparatus using concentration-jump relaxation techniques. Relaxation experiments were conducted at 24°C over a total dye concentration range of $1 \times 10^{-6} - 1 \times 10^{-5}$M. Under these conditions, appreciable amounts of monomer and dimer are present and the relaxation process can be followed spectrophotometrically. All dye solutions examined showed a single relaxation process. For a dimerization equilibrium, the following rate equations are applicable:

$$2M \underset{k_d}{\overset{k_f}{\rightleftharpoons}} D \qquad (7)$$

and the data can be analyzed in terms of the equation

$$\tau^{-2} = 8k_f^2/K_DC_T + k_f^2/K_D^2 \qquad (8)$$

where τ^{-2} is the reciprocal of the relaxation time squared, k_f and k_d are the forward and reverse rate constants in equilibrium (7) and all other terms have been previously defined. Figure 7 shows that the plot of τ^{-2} versus C_T is linear providing kinetic justification for the equilibrium assumed. Since k_f values obtained from the intercept of these plots are generally inaccurate,(57) the value of k_f was obtained from the slope. Using the determined K_D value of 1.1×10^7 M^{-1} the rate constants k_f and k_d are 3.24×10^6 $M^{-1}sec^{-1}$ and 0.29 sec^{-1}, respectively. Table 3 summerizes the thermodynamic and kinetic parameters determined for the dimerization of $CuTSPC^{4-}$ and other $MTSPC^{4-}$ systems. A comparison of the forward rate constants of Ni^{2+}, VO^{2+}, and Cu^{2+} shows them to be substantially larger than that of Co^{2+}. These results suggest that the more rapid dimer formation rates occur because there are no axial water molecules to interfere with the formation of the dimer which is not the case for the Co(II) system where axial ligand binding has been reported.(50,58-60) Moreover, similar dimer dissociation rates are observed for the Ni^{2+}, VO^{2+} and Cu^{2+} systems while substantially slower rates of dissociation occur with the Co^{2+} system. Thus, the greatest dimer stability is associated with the Co(II) system. Finally, similar K_D values are observed for the three aforementioned complexes as expected due to their similar rate constants but the dimerization constant of $CoTSPC^{4-}$ is essentially one order of magnitude smaller due to the relatively small formation rate constant of this complex. Although low K_D values are also reported for other tetrasulfonated metallophthalocyanines, no kinetics have been done on



DETERMINATION OF THE FORMATION AND DISSOCIATION RATE CONSTANTS IN THE $CuTSPC^{4-}$ SYSTEM AT 24° C

FIGURE 7

Table 3

Thermodynamic and Kinetic Parameters for the Dimerization of Some MTSPC^{4-} Systems

Metallophthalocyanine	log k_f ($M^{-1}sec^{-1}$)	logk_d (sec^{-1})	log K_D (M^{-1})	Temp (°C)	ΔH (kcal/mol)	ΔS (eu)	Ref.
CuTSPC^{4-}	6.51	-2.54	7.04	24	-0.76	-0.62	51**
VOTSPC^{4-}	6.65	-2.04	6.96	28	-8.7±3	2±5	9
*NiTSPC^{4-}	6.04	-2.74	6.78	25	-21	-31	16
CoTSPC^{4-}	3.11	-4.29	5.86	25	-14±0.9	-20±3	23

*Data obtained in aqueous 2% pyridine solution.

**Pertains to only the ΔH and ΔS values.

these systems; therefore, no attempt will be made here to discuss reasons for their relatively low dimerization constants from a kinetic point of view.

C. Ligand Binding Study

The axial binding of ligands by $CuTSPC^{4-}$ was studied spectrally. The addition of the ligands pyridine, thiocyanate, cyanide, cyanate, sulfide and azide to aqeuous $CuTSPC^{4-}$ solutions resulted in insignificant spectral changes compared to untreated aqueous $CuTSPC^{4-}$ samples. This result suggests that there is no spectral evidence that $CuTSPC^{4-}$ binds axial ligands in aqueous solution. These conclusions are in agreement with work done by other workers who found no evidence for binding in both their spectral and magnetic moment studies.(7,12) However, axial ligand binding does occur with other phthalocyanine complexes(38,61) especially in the iron system where several studies have been made.(62-67)

Some attempts were made to inspect the oxygen uptake properties of $CuTSPC^{4-}$ by examining spectra before and after purging the system with nitrogen. Slight spectral changes did occur but when oxygen gas was used, similar changes in the spectra occurred. Thus, no oxygen uptake occurred with $CuTSPC^{4-}$ as has been observed by other workers.(7,12) However, pH measurements taken prior to and after purging with nitrogen showed an increase in the sample pH suggesting removal of dissolved CO_2 in the system. Generally, the pH increased from 4.70 to 7.0 for the dye solutions and when purging was done with deionized water, a similar pH change occurred indicating no buffering action by the dye. Thus, reactions involving hydrolized species of CuTSPC^{4-} are highly unlikely.

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