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# Spectroscopic Study of Ni(II)-4, 4', 4'', 4''' – Tetrasulfophthalocyanine In Aqueous Solution

Issa Ishaq Jabra

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SPECTROSCOPIC STUDY OF  
Ni(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  
Issa Ishaq Jabra  
December 1978

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SPECTROSCOPIC STUDY OF  
Ni(II)-4,4',4'',4'''-TETRASULFOPHTHALOCYANINE  
IN AQUEOUS SOLUTION

Recommended July 27, 1978  
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Issa I. Jabra

SPECTROSCOPIC STUDY OF  
Ni(II)-4,4',4'',4'''-TETRASULFOPHTHALOCYANINE  
IN AQUEOUS SOLUTION

Issa Jabra

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Directed by: Dr. R. D. Farina, Dr. J. T. Riley, and  
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It was determined spectrally that a monomer-dimer equilibrium exists in aqueous solutions of Ni-TSPC<sup>4-</sup> over a concentration range of  $5 \times 10^{-8}$  -  $10^{-4}$  M. Equilibrium measurements were made under natural ionic strength conditions at 29°, 39° and 49°C. The values obtained for the equilibrium constants at 29°, 39° and 49°C were  $2.4 \times 10^8$ ,  $6.6 \times 10^7$  and  $2.9 \times 10^7 \text{ M}^{-1}$ , respectively. These results indicated that the equilibrium strongly favors dimer formation. This study also showed that nickel is second to copper in enhancing the dimerization of metallotetrasulfophthalocyanine complexes. However, metals in general inhibit dimer formation relative to the free ligand. The dimerization reaction of Ni-TSPC<sup>4-</sup> is exothermic with thermodynamic parameters of:  $\Delta G^\circ = -11.6$  kcal/mole,  $\Delta H^\circ = -20.9$  kcal/mole, and  $\Delta S^\circ = -31$  e.u. The dimerization process is thus favored from an energetic point of view despite the unfavorable entropy change.

Spectral measurements made on Ni-TSPC<sup>4-</sup> in aqueous-pyridine solutions in the concentration range of .5 - 6.0%

pyridine (by volume) indicated a dipyridinated dimer complex of Ni-TSPC<sup>4-</sup> was formed. Using a modified version of the Benesi-Hildebrand equation, the following equilibrium was proposed:  $D + 2Py = D(Py)_2$ . The overall equilibrium constants for this system at 15°, 21°, 30° and 40°C were 1.7, 1.9, 2.8, 3.6 and 4.4 M<sup>-2</sup>, respectively. The equilibrium reaction is endothermic with thermodynamic parameters of:  $\Delta G^\circ = 6.2$  kcal/mole,  $\Delta H^\circ = 6.9$  kcal/mole, and  $\Delta S^\circ = 25$  e.u. Thus, the equilibrium reaction was favored thermodynamically due to the favorable entropy change associated with the process.

Ligand studies indicated that only pyridine and polypyridine ligands bind to Ni-TSPC<sup>4-</sup> and cause a spectral change. This study also showed that Ni-TSPC<sup>4-</sup> cannot be used as an oxygen carrier in biological systems.

## INTRODUCTION

Phthalocyanines are organic macrocyclic compounds which are of industrial and biological interest. Their industrial importance reside with their electrical properties which make them quite suitable as semiconductors and photoconductors while their staining properties are of vital interest to the dye industries.<sup>1</sup> Phthalocyanines are of biological interest because they are structurally similar to the porphyrin molecule. Their ring system consists of four isoindole units linked by azo nitrogens, whereas the porphyrin has methine linkages instead.<sup>2</sup> Both are highly aromatic compounds having 18 pi electrons which conform with Hückel's  $4n+2$  rule of aromaticity. Both are amphoteric in that hydrogen 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. For these reasons, examining the properties of phthalocyanine systems could lend some insight into understanding the behavior of porphyrins in biological systems.

Hemes and chlorophylls are examples of porphyrins which aggregate both in aqueous and nonaqueous solvents.<sup>1,3,4</sup> Aggregation of hemes could be important in their role of oxygen carriers in biological systems while polymerization of chlorophylls could influence their role in photo-oxidation of water during photosynthesis.



### A. Polymerization of Metallophthalocyanines

Studies have been made on various chemical and physical properties of tetrasulfophthalocyanine (TSPC) and its metal derivatives (M-TSPC) which are soluble in water.<sup>4-10</sup> Solutions of phthalocyanine (PC), M-PC, TSPC and M-TSPC have been examined spectrally over extended concentration ranges in various solvents at room temperature.<sup>1,4,5,7-12</sup> Many follow Beer's Law in organic solvents but large deviations from Beer's Law occur in aqueous solutions which has been attributed to aggregation.<sup>10,13</sup> Most studies made on the polymerization properties of M-TSPC systems have been limited to the dimerization stage by examining dilute solutions. The spectra of these solutions in concentration ranges of approximately  $10^{-7}$  -  $10^{-5}$  M reveal an isosbestic point and two bands at the far end of the visible range, which has been attributed to a monomer-dimer equilibrium. The monomer band in these systems is always located at the longer wavelength while the other band has been assigned to the dimer. High concentrations appear to favor formation of the dimer while the converse is true for the monomeric species. When these solutions are diluted, the dimer dissociates to form monomer. Similar behavior has been displayed by porphyrins and dye compounds which aggregate in solution.<sup>7-16</sup> Higher aggregates form in these systems when the dye concentration exceeds  $10^{-5}$  M as evidenced by a single absorption band which undergoes a spectral shift to lower wavelengths. This band appears to broaden and lose intensity compared to the monomer and dimer bands.<sup>13,16,17</sup> Spectral studies show that increasing the



temperature favors the formation of the monomer at the expense of the dimer since part of the heat supplied can be used to dissociate the dimer. It has been reported that using very dilute solutions and high temperatures frequently allows the equilibrium to be driven completely to the monomer stage.<sup>7-9</sup> For example, the monomer-dimer equilibrium of a  $10^{-7}$  M Co-TSPC<sup>4-</sup> aqueous solution was shifted completely to the monomer by raising the temperature to 81°C.<sup>8a</sup> The relatively high negative charge on the monomeric species makes the polymerization process very sensitive to ionic strength effects in that added electrolytes favor polymer formation. Bernauer and Fallab report that the addition of salts to several metallophthalocyanines convert the monomeric species into the dimeric species.<sup>18</sup> Small amounts of NaClO<sub>4</sub> tend to stabilize the dimer of Fe-TSPC<sup>3-</sup> while large amounts of NaClO<sub>4</sub> cause further aggregation.<sup>7</sup> Salt effects have also been examined on the Co-TSPC<sup>4-</sup> system using electronic spectra and concentration-jump relaxation techniques.<sup>8a</sup> Similar salt effects were found in porphyrin systems.<sup>19,20</sup> Addition of acid or base favors the formation of dimer since they behave like salts. The proton prevails in acid solutions while the hydroxide ion acts as the anion in alkaline solution.<sup>9</sup> Under slightly acidic or basic conditions, in a 1:1 DMF:H<sub>2</sub>O mixture (by volume), the Mn-TSPC<sup>3-</sup> system was found to form mixed hydroxide complexes and the dinuclear compound, [(H<sub>2</sub>O)Mn(TSPC)-O-(TSPC)Mn(OH)]<sup>9-</sup>.<sup>21</sup>

Several studies on metallophthalocyanine systems indicate that addition of organic solvents such as methanol, ethanol, dimethylsulfoxide, and pyridine cause the dimer to

dissociate with a resulting shift of the equilibrium to the monomer.<sup>5,7,9</sup> Very few studies on M-TSPC have been conducted in pure organic solvents.<sup>22</sup> Spectral studies made on the copper(II), VO(II), and Zn(II) complexes of tetraalkylphthalocyanine (TAPC) in benzene show dimerization occurs.<sup>1</sup> Similar behavior was displayed by Cu-TAPC in various other organic solvents.<sup>11</sup> The dimerization of Cu-TAPC in various organic solvents decreased as follows: carbon tetrachloride > benzene > toluene > chloroform > dioxane > DHF > THF. It was found that the aggregation tendency of this dye is diminished in solvents where the dye is more soluble.

It has been proposed for the Co-TSPC<sup>4-</sup> system that the dimer in solution is formed by the overlapping of extended pi electron clouds of the highly conjugated TSPC molecules of two parallel monomeric species staggered and stacked above one another.<sup>6</sup> The calculated distance between the two monomers of the Co-TSPC<sup>4-</sup>, Cu-TSPC<sup>4-</sup>, and VO-TSPC<sup>4-</sup> dimers<sup>6,23</sup> in solution were 5 Å and 4.3 Å and 4.5 Å, respectively, while that of phthalocyanine<sup>24</sup> and Ni-PC<sup>25</sup> dimers in the solid state were both reported to be 3.38 Å. Comparing these values with that of Co-TSPC<sup>4-</sup> obtained in solution suggests that the separation between monomer units in the dimers of M-TSPC systems may lie between 3.38 and 5 Å.

In order to form the dimer, the dye-dye interaction must be strong enough to overcome any forces which would favor dimer dissociation. A low dielectric constant of the solvent enhances dissociation due to the reduced screening of the dye-dye interaction by the solvent.<sup>1</sup> It has been

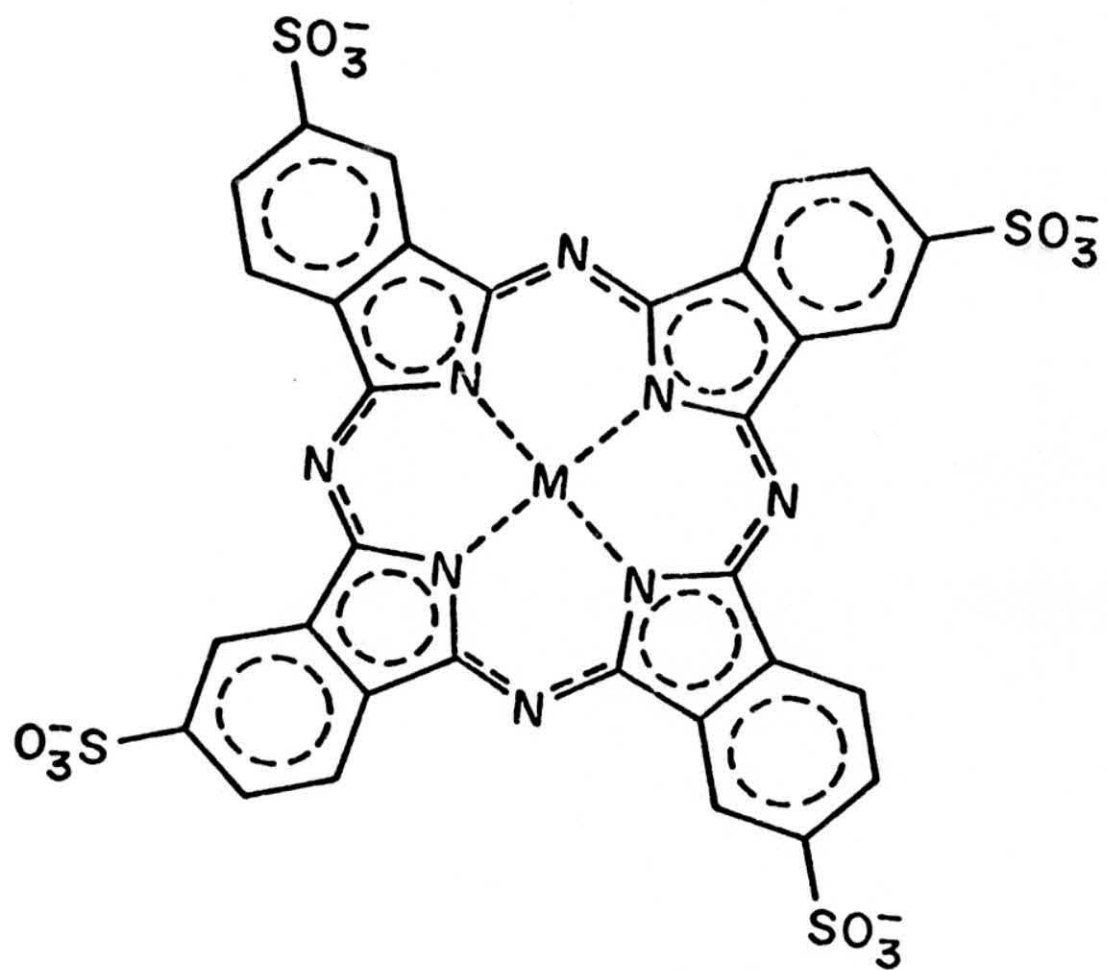
proposed that in solvents of low dielectric constant, the dye-dye interaction is the driving force for dimerization.<sup>26</sup> In the case of water, the dye-dye interaction is probably not the major force causing the monomer to associate. Instead, strong solvent-solvent interactions are postulated which tend to exclude the dye molecules from solution causing them to aggregate.<sup>1</sup> Frequently, aggregation in organic solvents of relatively high dielectric constant is reduced or is minimized which suggests that solvation interferes with the aggregation. In such solvents, aggregates are stable only at low temperatures under conditions of high viscosity.<sup>13</sup> Other factors influencing dimerization have been reported such as the additive forces of Van der Waal and intermolecular hydrogen bonding between the monomeric species.<sup>27</sup>

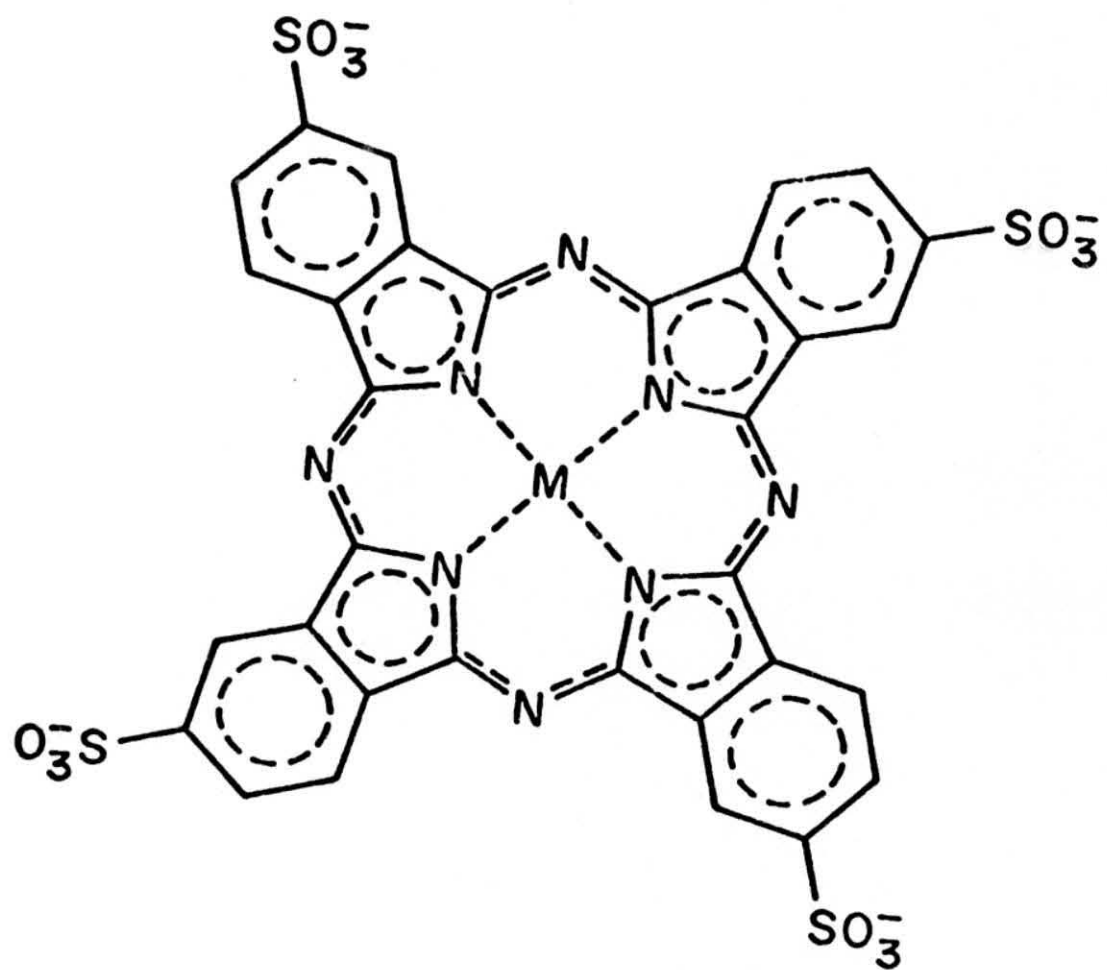
Although there have been several studies made on substituted and unsubstituted phthalocyanine complexes of Co(II),<sup>4,6,8,12,18,28</sup> Cu(II),<sup>1,4,11,18,23,29</sup> VO(II),<sup>9,11,23</sup> Zn(II),<sup>11,18,30,31</sup> Fe(II),<sup>7,10,28,31</sup> Mn(II),<sup>28,31</sup> Mn(III),<sup>21</sup> Cr(II),<sup>31</sup> Ni(II),<sup>4,20,28,30,31</sup> and  $H_2TSPC^{4-}$ <sup>4,5,18</sup> in aqueous solution or organic solvents, nothing has been reported on the properties of  $Ni-TSPC^{4-}$  in aqueous solution. Therefore, the first part of this study deals with the polymerization properties of  $Ni-TSPC^{4-}$  in aqueous solution where a comparison can be made with that of other M-TSPC systems. A typical structure of M-TSPC is presented in Figure 1.

### B. Ligand Binding Studies

It is well known that metals provide coordination sites

Figure 1. Typical Structure of a Tetrasulfonated  
Metallophthalocyanine Complex.





in many naturally occurring biological substances containing macrocyclic compounds such as the metalloporphyrins. Their biological functions often are influenced by the nature of, or the exchange of, labile extraplanar ligands as well as the variable oxidation states of the metal.<sup>32</sup> Therefore, ligand binding studies may provide more insight into the behavior of these species in biological systems. The axial ligand binding properties of phthalocyanines have not been explored to the extent of the porphyrins. Studies which have been made on phthalocyanine complexes have dealt mainly with Co-TSPC<sup>4-</sup>, Mn-PC, and Fe-PC. Weber and Busch investigated the addition of several ligands such as pyridine, imidazole, benzimidazole, nitrite and cyanide to Co-TSPC<sup>4-</sup> and observed that the strongly binding ligands, cyanide and imidazole, facilitate oxidation of the Co-TSPC<sup>4-</sup> by atmospheric oxygen to Co(III) derivatives.<sup>28</sup> Spectral studies made on the reaction of Mn-PC with pyridine in the absence of air show that Mn-PC(Py)<sub>2</sub> forms, while exposure to air allows the dinuclear species of oxygen (MnPCPy)<sub>2</sub>O to form.<sup>33</sup> In the Fe-PC system, the exchange of imidazole, pyridine and other nitrogenous bases for solvent in dimethylsulfoxide occurs.<sup>35-37</sup> Moreover, some studies investigated the addition of aromatic nitroso compounds and hydrochloric acid to this complex.<sup>38,39</sup> Kinetic studies have also been made on the addition of ligands to Fe-PC.<sup>40,41</sup> A survey of the literature shows there has been no ligand binding studies made on Ni-TSPC<sup>4-</sup>. Therefore, the second part of this study pertains to axial ligand

coordination on this extraplanar complex. The results of this work will be compared with other analogous nickel compounds.



## EXPERIMENTAL

This section elaborates on the materials used, the apparatus needed, sample handling, spectral and equilibrium measurements and the preliminary experiments.

### A. Materials

#### 1. Ni-TSPC<sup>4-</sup>

The tetrasodium salt of Ni-TSPC<sup>4-</sup> used in this research was derived from two sources. One source of the salt was obtained from Charles J. Hunt, at Western Kentucky University, who prepared it by literature methods<sup>28</sup> while the other was a gift from Dr. Daryle H. Busch, of Ohio State University. The dark blue solid was kept in a vacuum dessicator to prevent the absorption of atmospheric moisture. The spectral properties of both salts compared well with literature values.<sup>4</sup>

#### 2. Pyridine

Reagent grade pyridine purchased from Matheson, Coleman, and Bell was further purified by leaving the pyridine over potassium hydroxide for several days. The liquid was then refluxed over potassium hydroxide for half an hour before being distilled. The fraction boiling at 115.0°C was collected in brown bottles and stored over Linde 4A molecular sieves.<sup>42,43</sup>

### 3. Dimethylsulfoxide

This research grade solvent was purchased from J. T. Baker Chemical Company and used with no further purification.

#### B. Apparatus

##### 1. Cary Model 14 Recording Spectrophotometer

The spectral and equilibrium measurements were obtained on a Cary Model 14 recording spectrophotometer which can be used in the ultraviolet, visible and near infrared spectral regions. The spectral measurements in this study were limited to a range of 300-700 nm (the visible region). 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 bath was used to pump water through the sample jacket via 1/4 inch tygon tubing. Using this assembly permits the temperatures of the solution in the spectral cell to be maintained within  $\pm 0.03^\circ\text{C}$  at temperatures of  $25^\circ$  to  $80^\circ\text{C}$ . For work at lower temperatures, ice was added to a bucket of water which was fed to the Haake circulator via a vertical centrifugal immersion pump, Model 2G159 manufactured by Gelber Pump Company. Connections to and from the pump consisted of 1/4 inch tygon tubing.

Cylindrical quartz cuvette cells of 0.01, 0.10, 0.20, 0.50, 1.00 and 10.00 cm path lengths were used for the spectrophotometric measurements. When very small absorptions

could not be adequately measured with the 10.00 cm spectral cells on the 0 - 2.0 slidewire, the more sensitive slidewire with a 0 - 0.2 absorption range was utilized.

### 2. Portable Microprobe Thermometer

The temperature of the dye solution was accurately measured by using a portable microprobe thermometer, Model Bat-4 manufactured by Bailey Instruments Company, Inc. The liquid immersion probe of the thermometer is 0.025 inches in diameter and is 3 feet in length. The probe is totally encased in a chemical-resistant teflon sheath. The immersion probe, Model No. 8506-75, and the portable thermometer were purchased from Cole Parmer Instrument Company. The diameter of the probe was selected so that the probe can be placed in the spectral cell containing the dye solutions for better accuracy of the temperature measurements. The compartment was covered to allow the temperature of the solution to equilibrate faster and to reduce excessive heat losses to the atmosphere at the higher temperature conditions.

### 3. Balance

A digital analytical balance was used for the weight measurements. The instrument has a 100 mg - 200 g. range with an accuracy of  $\pm 0.10$  mg. The analytical balance, Model 2402 was made in Gottingen, Germany by Sartorius-Werke AG.

### C. Sample Handling

A fresh stock solution of  $10^{-5}$  M Ni-TSPC<sup>4-</sup> was prepared prior to each experiment. The stock solution was

diluted to obtain a series of solutions at different concentrations. In order to dissolve the salt completely and obtain a homogeneous mixture, all solutions were heated and stirred for approximately 20 minutes. When the solution in the spectral cell was heated above 50°C, air bubbles formed which interfered with the spectral measurements. Therefore, it was necessary to preheat and de-aerate the solutions with nitrogen or argon for thirty minutes to remove the air bubbles. Volumetric flasks and spectral cells were covered at all times to prevent evaporation of the solutions. On a few occasions, the commercial teflon covers for the spectral cells created problems. When the dye in the 10.0 cm spectral cell was heated above 50°C, the teflon covers expanded and sealed the cell. At about 70°C, the pressure resulting from the expansion of the solution can blow out one of the cell windows (actually occurred twice). Consequently, glass stoppers or parafilm should be used when performing spectral studies at high temperatures. Spectral cells were cleaned with 0.1 M HCl then flushed with deionized distilled water and dried prior to use. The position of the spectral cells were checked prior to each spectral measurement to ensure that the cells were not tipped to one side. Improperly placed cells can interfere with the spectral measurements.

#### D. Spectroscopic Measurements

This section is divided into two parts. The first part discusses the spectral measurements made on the Ni-TSPC<sup>4-</sup> system in aqueous and in aqueous-pyridine solutions.

The second part deals with the equilibrium measurements made on Ni-TSPC<sup>4-</sup> in these two media.

### 1. Spectral Measurements

Spectral measurements were made on aqueous Ni-TSPC<sup>4-</sup> solutions in the concentration range of  $2 \times 10^{-8}$  -  $10^{-4}$  M over a wavelength range of 300-700 nm. An isosbestic point at 644 nm and two bands at the far end of the visible range were observed which has been attributed to a monomer-dimer equilibrium. The spectrum of this system was similar to that of other metallophthalocyanine systems.<sup>8,19,18</sup> This system like all the others has the band at the longer wavelength (666 nm) assigned to the monomeric species, while the band at the shorter wavelength (630 nm) has been ascribed to the dimer. Since the absorption bands of the monomer and dimer overlap, it was necessary to shift the monomer-dimer equilibrium completely in each desired direction in order to obtain the molar absorptivities of each species. For the monomer, this was accomplished by raising the temperature of a very dilute ( $2 \times 10^{-8}$  M) solution until no further increase in absorbance was observed at the monomer absorption maximum. The temperature at which no increase in absorption occurred was 85°C. The calculated value of the molar absorptivity of the monomer,  $\epsilon_M$ , at wavelength 666 nm is  $1.55 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The molar absorptivity of the monomer was also obtained at 25°C by adding DMSO to an aqueous solution of  $2 \times 10^{-8}$  M Ni-TSPC<sup>4-</sup> until no further increase in the monomer absorption band was detected. The results were in good agreement with each other and the literature value.<sup>4</sup>

These studies show that over a temperature range of 25°-85°C,  $\epsilon_M$  does not vary appreciably.

The complete shift in equilibrium to the dimer was obtained by decreasing the temperature of a concentrated ( $10^{-4}$  M) solution until no further increase in absorbance at the dimer absorption maximum was observed. This occurred at 11°C. The calculated value of the molar absorptivity of the dimer,  $\epsilon_D$ , at wavelength 630 nm is  $1.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . The  $\epsilon_D$  value at 29°C was also obtained by plotting  $\log (1/C_T)$  versus  $\log \epsilon$  for a concentration range of  $5 \times 10^{-8}$  -  $1 \times 10^{-5}$  M ( $C_T$  values) and extrapolating to infinite concentration, i.e.,  $1/C_T \rightarrow 0$ , where  $\epsilon = \epsilon_D$ . This result was in good agreement with the value obtained by decreasing the temperature. The results of the spectral measurements of Ni-TSPC<sup>4-</sup> in aqueous solution are summarized below.

	$\lambda(\log \epsilon_{\max})$	$\lambda(\log \epsilon_{\max})$	$\lambda(\log \epsilon_{\max})$
monomer	666 (5.19)	604 (4.72)	324 (5.08)
dimer	650 (sh)*	630 (5.08)	333 (4.85)

\*All wavelength units are in nanometers with shoulder designated sh.

Spectral measurements were also made on Ni-TSPC<sup>4-</sup> in aqueous-pyridine solutions in a concentration range of  $2 \times 10^{-7}$  -  $1 \times 10^{-5}$  M. A pyridine concentration range of 0.5 - 6.0% (by volume) was used. However, the specific concentration range of pyridine used was dependent on the total dye concentration in order to ensure that no, or negligible amounts of, monomer are present. The spectrum of these



solutions revealed that another equilibrium was established since a new absorption maximum and isosbestic point (652 nm) was formed. The complete visible absorption spectrum consists of two bands, that of the dimer with an absorption maximum of 630 nm and that of a pyridinated species with a band at 672 nm. Using a modified version of the Benesi-Hildebrand equation, the molar absorptivity of the pyridinated species,  $\epsilon_{DL_2}$ , was obtained.<sup>44,45</sup>

## 2. Equilibrium Measurements

Equilibrium constants were obtained from spectral measurements made on Ni-TSPC<sup>4-</sup> in aqueous solution over a concentration range of  $5 \times 10^{-8}$  -  $1 \times 10^{-5}$  M at their natural ionic strengths. Spectral cells of 0.2, 0.5, 1.0 and 10.0 cm path lengths ( $l$ ) were used with the appropriate dye concentrations so that the product of  $lC_T$  was constant. The spectra revealed an isosbestic point at 644 nm. When the solution was diluted, the positions of the absorption bands in the spectrum remained the same, but their intensities varied. The amplitude of the monomer band increased at the expense of the dimer band (see Figure 2) which lends support for the monomer-dimer equilibrium. Aggregation beyond the dimer stage was not observed in this dye concentration range.

The effect of temperature on the monomer-dimer equilibrium was also studied. Spectra of a  $5 \times 10^{-6}$  M solution of Ni-TSPC<sup>4-</sup> at natural ionic strength were taken at four different temperatures: 30°, 50°, 60°, and 70°C (see Figure 3). The spectra revealed the same isosbestic point with high temperatures favoring the monomer at the expense

Figure 2. Concentration Effect on the Monomer-Dimer  
Equilibrium of Ni-TSPC<sup>4-</sup> at 40°C.



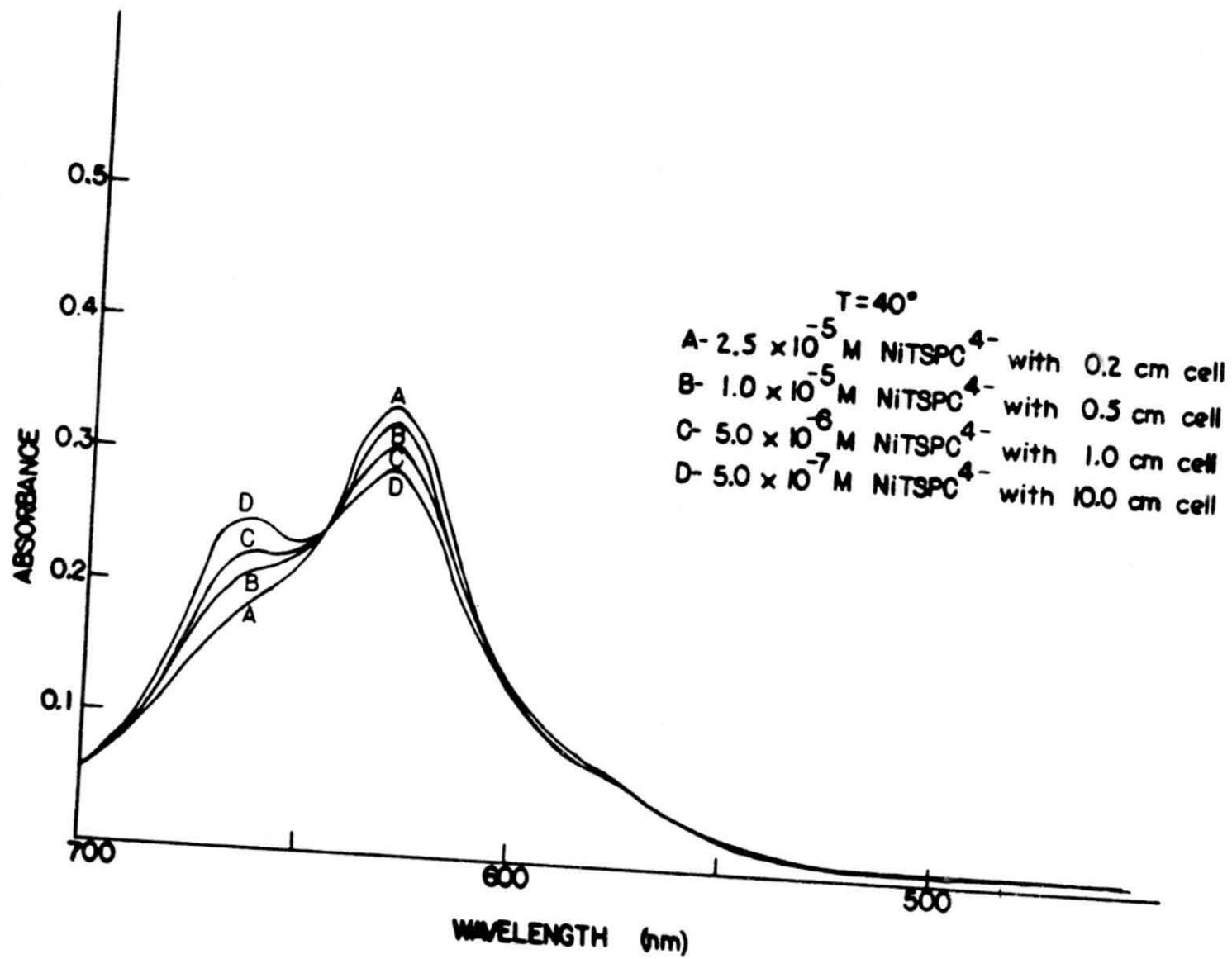
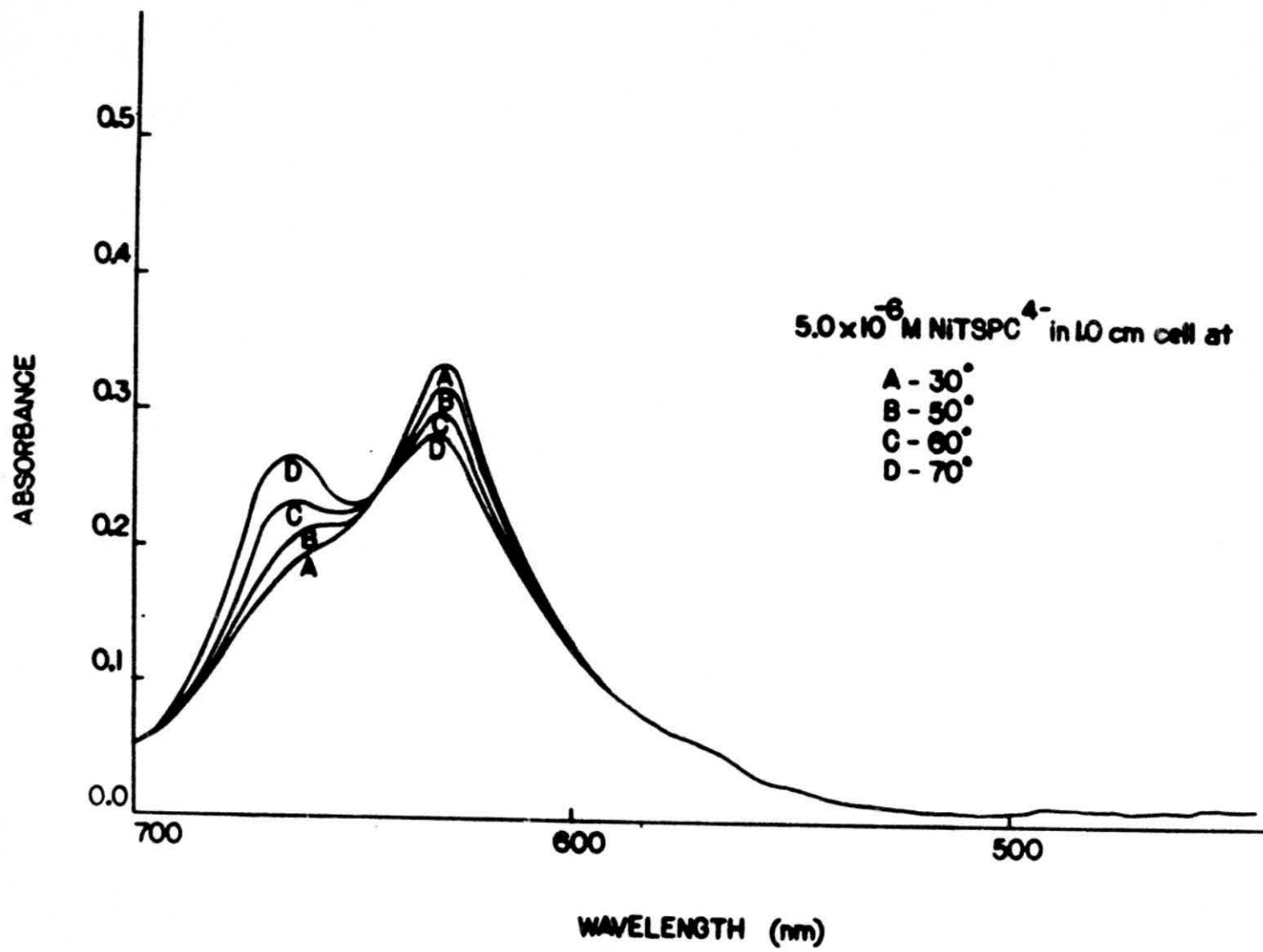


Figure 3. Temperature Effect on the Monomer-Dimer  
Equilibrium of Ni-TSPC<sup>4-</sup>.



of the dimer. The equilibrium constant was obtained by using Beer's Law, the conservation of mass, and the equilibrium constant expressions (see Discussion and Results).

Equilibrium measurements were also made on aqueous solutions of  $\text{Ni-TSPC}^{4-}$  in the presence of pyridine over the same concentration ranges used to obtain the molar absorptivity of the pyridinated species. Figure 4 shows the new isosbestic point at 652 nm obtained by using a  $10^{-5}$  M  $\text{Ni-TSPC}^{4-}$  solution in a pyridine concentration range of 1-5% by volume. As can be seen in the figure, the intensity of the absorption band of the pyridinated species increases at the expense of the dimer when the pyridine concentration is increased. The equilibrium constant was determined graphically using a modified form of the Benesi-Hildebrand equation.<sup>44,45</sup>

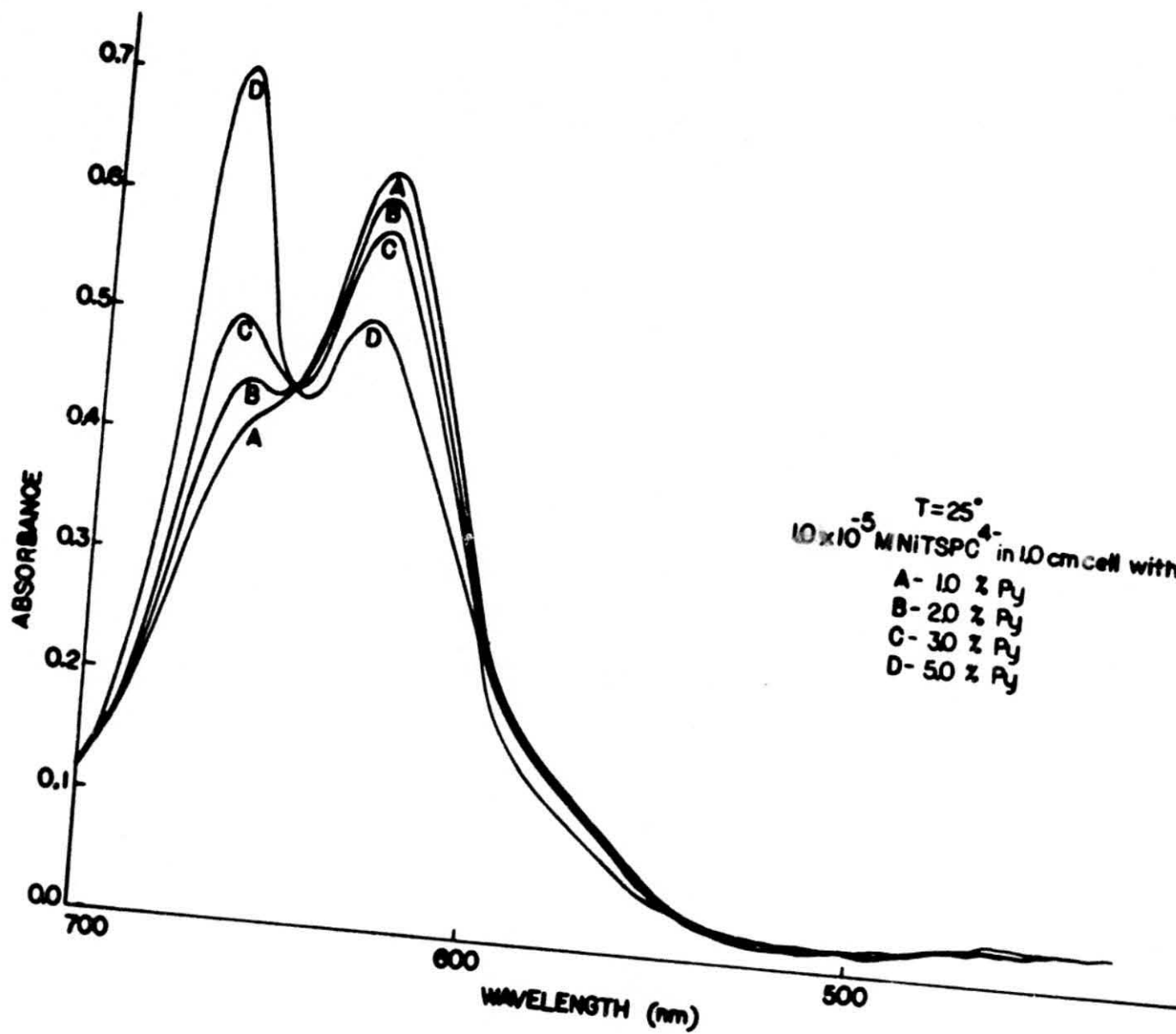
#### E. Preliminary Experiments

This section includes other pertinent experiments which have not been discussed.

##### 1. Addition of Ligands

No spectral changes were observed for a number of ligands added to  $\text{Ni-TSPC}^{4-}$  in aqueous solution. These include: potassium cyanate, sodium azide, piperdine, ammonia, sodium cyanide, sodium isothiocyanate, imidazole, diethylenetriamine, ethylene carbonate cyclic ester, tetraethylenepentamine, tetrasodium salt of EDTA and triethylenetetramine. Only pyridine, bipyridine, and tripyridine gave spectral evidence for ligand addition. Various gases were

Figure 4. Effect of Pyridine on the Monomer-Dimer  
Equilibrium of Ni-TSPC<sup>4-</sup> at 25°C.



also added to the system but none appeared to react with the dye. The gases used were oxygen, nitrogen, carbon monoxide, and argon. If syringe needles are used, they should be pretreated in dilute HCl (0.1 M) to prevent reaction with the dye. Platinum needles may be used without pretreating with dilute acid.

## 2. Blood Serum

The blood serum was obtained by venipunctures from different human male and female donors in the Bowling Green-Warren County Hospital. No attempt was made to filter the pooled serum to a constant protein level. However, the serum was further purified by removing the remaining suspended materials via centrifuging at 0°C and 3000 RPM for twenty minutes. The centrifuge is a IEC-PR-J model with a rotary number 269 head size manufactured by Damon/IE Division.

Various concentrations of Ni-TSPC<sup>4-</sup> ( $5 \times 10^{-7}$ ,  $5 \times 10^{-6}$  and  $1 \times 10^{-5}$  M) in blood serum were prepared and examined spectrophotometrically. The spectra of these solutions showed a single broad band in the same vicinity as that of the dimer in aqueous solution. Due to the complexity of this system in blood serum, no further studies were made.

## 3. Kinetic Measurements

A few kinetic measurements were attempted on the stopped-flow apparatus using concentration-jump relaxation methods outlined elsewhere.<sup>8,9</sup> The equilibrium of Ni-TSPC<sup>4-</sup> in aqueous solution strongly favors the dimer so that the stopped-flow apparatus could not detect any spectral changes

associated with the dilution after mixing. However, preliminary kinetic measurements made on Ni-TSPC<sup>4-</sup> in aqueous-pyridine media show that the spectral changes resulting from the dilution perturbation could possibly be followed.



## RESULTS AND DISCUSSION

The results and discussion of this study is divided into two parts. The first part deals with the dimerization of Ni-TSPC<sup>4-</sup> in aqueous solution while the other part is concerned with the ligand binding properties of this complex.

### A. Dimerization of Ni-TSPC<sup>4-</sup>

The presence of an isosbestic point at 644 nm for the superimposed spectra of Ni-TSPC<sup>4-</sup> aqueous solutions in the concentration range of  $5 \times 10^{-8}$  -  $10^{-5}$  M is consistent with a monomer-dimer equilibrium which has been observed in other M-TSPC<sup>4-</sup> systems.<sup>7-9, 29</sup> Assuming an equilibrium exists between monomer (M) and dimer (D), the following equations are applicable:

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

$$K_D = \frac{C_D f_D}{(C_M f_M)^2} \quad (2)$$

where  $C_D$  and  $C_M$  are the equilibrium concentrations of the dimer and monomer, respectively, with  $f_D$  and  $f_M$  their respective activity coefficients. However, in dilute solutions, the activity coefficients are unity yielding equations (3) and (4):

$$\lim_{C_T \rightarrow 0} \frac{f_D}{f_M^2} = 1 \quad (3)$$

therefore:

$$K_D = \frac{C_D}{C_M^2} = Q_D \quad (4)$$

where  $Q$  is defined as the concentration quotient. The concentrations of monomer and dimer present in the equilibrium at a given temperature can be obtained from the following set of equations:

$$C_T = C_M + 2 C_D \quad (5)$$

$$A/l = \epsilon_M C_M + \epsilon_D C_D \quad (6)$$

where  $C_T$  is the total concentration of the Ni-TSPC<sup>4-</sup>,  $l$  is the optical path length and  $A$  is the absorbance of the solution at a given wavelength. Combining equations (5) and (6) yield the following:

$$C_M = (2 A/l - \epsilon_D C_T) / (2 \epsilon_M - \epsilon_D) \quad (7)$$

$$C_D = \frac{C_T - C_M}{2} \quad (8)$$

In order to obtain the dimerization constant,  $K_D$ , in this system at a given temperature,  $\epsilon_M$  and  $\epsilon_D$  must be determined. Due to the difficulty in obtaining  $f_M$  and  $f_D$ , all equilibrium measurements were made at natural ionic strength conditions from which the concentration quotients were extrapolated to infinite dilution to obtain the dimerization constant.  $C_D$  and  $C_M$  can be calculated from equations (7) and (8) since  $A$ ,  $l$  and  $C_T$  are known experimentally while  $\epsilon_M$  and  $\epsilon_D$  are obtained by methods described in the experimental section. Tables 1, 2 and 3 list the experimental data used in obtaining the  $Q$  values at 29°, 39° and 49°C. The experimental

Table 1  
 Concentration Quotients of the Ni-TSPC<sup>4-</sup> Dimerization  
 in Aqueous Solution at 29°C

A (10 <sup>2</sup> )	C <sub>T</sub> (10 <sup>7</sup> ) (M)	C <sub>M</sub> (10 <sup>8</sup> ) (M)	C <sub>D</sub> (10 <sup>7</sup> ) (M)	Q <sub>D</sub> (10 <sup>-7</sup> ) (M <sup>-1</sup> )
35.60	100.00	44.80	47.80	2.38
18.80	50.00	30.40	23.50	2.54
7.70	20.00	13.60	9.32	5.04
3.87	10.00	6.46	4.65	9.60
1.98	5.00	3.84	2.31	15.70
0.47	1.00	1.38	0.43	22.60
0.27	0.50	0.96	0.21	22.90

Note: The  $\epsilon$  values of monomer and dimer are  $1.55 \times 10^5$   
 and  $6.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, at 666 nm.

Table 2

Concentration Quotients of the Ni-TSPC<sup>4-</sup> Dimerization  
in Aqueous Solution at 39°C

A (10 <sup>2</sup> )	c <sub>T</sub> (10 <sup>7</sup> ) (M)	c <sub>M</sub> (10 <sup>8</sup> ) (M)	c <sub>D</sub> (10 <sup>7</sup> ) (M)	Q <sub>D</sub> (10 <sup>-7</sup> ) (M <sup>-1</sup> )
36.81	100.00	54.50	46.90	1.58
19.25	50.00	34.00	23.30	2.02
8.25	20.00	18.00	9.10	2.81
4.48	10.00	11.80	4.41	3.17
2.35	5.00	6.80	2.16	4.67
0.61	1.00	2.48	0.38	6.11
0.35	0.50	1.62	0.17	6.44

Note: The  $\epsilon$  values of monomer and dimer are  $1.55 \times 10^5$   
and  $6.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, at 666 nm.

Table 3

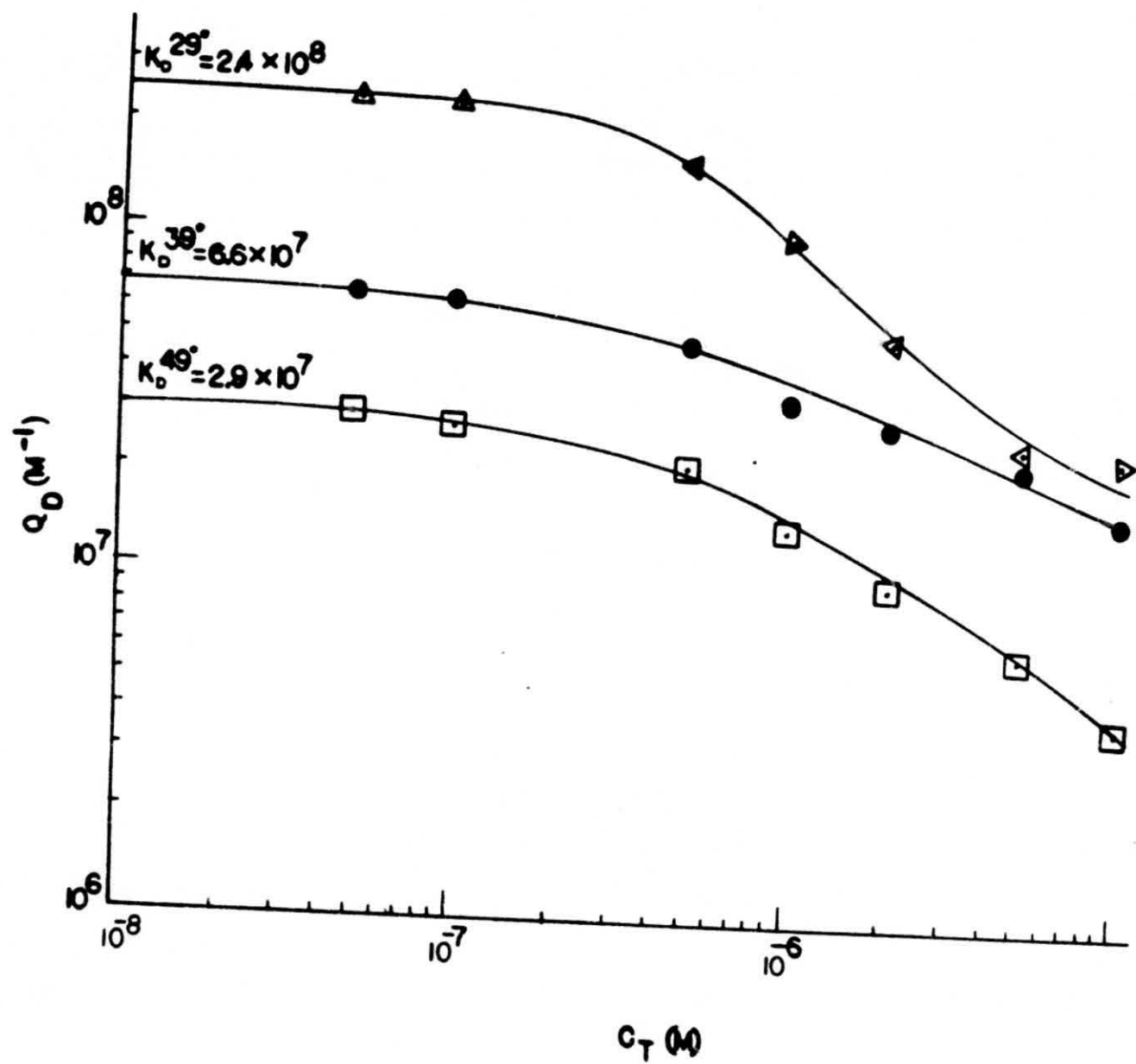
Concentration Quotients of the Ni-TSPC<sup>4-</sup> Dimerization  
in Aqueous Solution at 49°C

A (10 <sup>2</sup> )	C <sub>T</sub> (10 <sup>7</sup> ) (M)	C <sub>M</sub> (10 <sup>8</sup> ) (M)	C <sub>D</sub> (10 <sup>7</sup> ) (M)	Q <sub>D</sub> (10 <sup>-7</sup> ) (M <sup>-1</sup> )
43.50	100.00	108.00	46.10	0.40
22.00	50.00	59.20	22.00	0.63
9.59	20.00	28.70	7.88	0.96
5.15	10.00	17.20	4.14	1.40
2.72	5.00	9.76	2.01	2.11
0.74	1.00	3.48	0.33	2.69
0.43	0.50	2.20	0.14	2.89

Note: The  $\epsilon$  values of monomer and dimer are  $1.55 \times 10^5$   
and  $6.00 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ , respectively, at 666 nm.

Q values are graphed and extrapolated to infinite dilution as shown in Figure 5. The dimerization constants at 29°, 39° and 49°C are  $2.4 \times 10^8$ ,  $6.6 \times 10^7$ , and  $2.9 \times 10^7 \text{ M}^{-1}$ , respectively.

Figure 5. Determination of  $K_D$  from Concentration Quotients  
at Different Temperatures.





The large dimerization constants indicate that the equilibrium favors the dimer. The decrease of  $K_D$  with temperature shows that the dimerization process is exothermic. This is consistent with the dimerization reaction which involves bonding between monomeric units in forming the dimer with no axial ligands present on the monomeric species. The Gibbs-Helmholtz plot yields a  $\Delta H^\circ$  value of  $-20.9$  kcal/mole. Since the enthalpy change also includes the heats of solution for monomer and dimer which are unknown,  $\Delta H^\circ$  cannot be interpreted in terms of bond energy or heat of dissociation. The negative value for the entropy change ( $-31$  e.u.) is consistent with a decrease in the number of species in proceeding from reactants to products and hence an increase in the order within the system. Despite the unfavorable entropy change, the formation of dimer is favorable from an energetic point of view ( $\Delta G^\circ = -11.6$  kcal/mole at  $29^\circ\text{C}$ ). The thermodynamic results for the dimerization of  $\text{Ni-TSPC}^{4-}$  in aqueous solution are presented in Table 4.

Table 5 lists the dimerization constants for a number of tetrasulfonated metallophthalocyanine complexes including the ligand itself. An examination of Table 5 reveals that the stability of the dimer decreases in the order:  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{H}^+ > \text{Zn}^{2+} \sim \text{VO}^{2+} > \text{Fe}^{3+} > \text{Co}^{2+}$ . All of the complexes have neutral centers except the  $\text{Fe}^{3+}$  complex which is 1. The dimerization constant varies by nearly two orders of magnitude within the series. The greater stability of the  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  dimers may be due to the lack of axial ligands ( $\text{H}_2\text{O}$ ) present on their monomer units which would

Table 4  
Thermodynamic Parameters for the Ni-TSPC<sup>4-</sup>  
Dimerization Process

Temp (°C)	$K_D \times 10^7$ (M <sup>-1</sup> )	$\Delta G^\circ$ (kcal/mole)	$\Delta H^\circ$ (kcal/mole)	$\Delta S^\circ$ (e.u.)
29°	24.0	-11.6	-20.9	-31
39°	6.6	-11.2	-20.9	-31
49°	2.9	-10.7	-20.9	-31

Table 5

Dimerization Constants of Some Tetrasulfonated  
Metallophthalocyanines

T (°C)	Metal	Log $K_D$ (M <sup>-1</sup> )
61°	Cu <sup>2+</sup>	7.2
58°	Ni <sup>2+</sup>	7.1*
62°	H <sup>+</sup>	7.0
58°	Zn <sup>2+</sup>	6.0
60°	VO <sup>2+</sup>	6.0
58°	Co <sup>2+</sup>	5.3*
60°	Fe <sup>3+</sup>	5.9

\*Obtained at zero ionic strength while all other values were reported at natural or low ionic strength.

interfere with the formation of their dimer. This point of view is also supported by the crystal field theory which predicts that  $d^8$ ,  $d^9$ , and  $d^{10}$  systems form stable square planar monomeric species while the octahedral geometry is more favored for the others. If this is so, similar dimerization constants should be obtained for all of the other metals which is not the case. The dimerization constants of  $VO^{2+}$  and  $Fe^{3+}$  are appreciably larger than  $Co^{2+}$  indicating other factors are involved. In the case of iron, the overall charge on the monomeric species is reduced by one compared to cobalt (and the others) which would tend to reduce the coulombic effects upon dimer formation and lead to a larger dimerization constant. The greater stability constant of the  $VO^{2+}$  dimer is interesting. It is tempting to suggest that the structural features of the dimer in this system are different. Since only one open site on the metal is available, dimer formation is expected to be difficult. However, the possibility of metal-metal bonding or oxygen bridging (VOV) would tend to stabilize the dimer and hence increase the dimerization constant. Oxygen bridging is known to occur in electron transfer reactions involving vanadium complexes.<sup>9</sup> However, at this stage, this would be only speculation as no structural data on the vanadium dimer in solution have been obtained. Presently, the results suggest that metals in general inhibit or destabilize dimer formation relative to the free ligand.

A comparison of the dimerization constant of the  $Ni-TSPC^{4-}$  complex with  $Ni-TPPC_4$ ,<sup>46</sup>  $Ni(En-Proto-IX-DME)$ <sup>47</sup> and  $Ni(Meso-IX-DME)$ <sup>15</sup> porphyrins (see Table 6) indicate that

Table 6

Dimerization Constants of Ni(II) Porphyrins and  
the Ni(II)-TSPC<sup>4-</sup> Complex

Complex	T (°C)	$\mu$ (M)	Solvent	log K <sub>D</sub>
Ni-TPPC <sub>4</sub>	25	0.10	H <sub>2</sub> O	5.20
Ni(En-Proto-IX-DME)	25	0.02	5% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	6.90
	25	0.02	10% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	6.20
	25	0.02	15% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	5.80
	25	0.02	20% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	5.30
	25	0.02	25% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	4.75
	25	0.02	30% C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O	4.25
Ni(Meso-IX-DME)	30	Natural	CHCl <sub>3</sub>	1.79
Ni-TSPC <sup>4-</sup>	29	0	H <sub>2</sub> O	8.38

the greater dimer stability is associated with the metallo-phthalocyanine complex. Perhaps this difference resides with the fact that in tetrasulfophthalocyanine, nickel(II) is located in the plane of the ring while in the others it is located above the porphyrin plane. Therefore, in the phthalocyanine complex, the metal  $d^8$  electrons can interact more strongly with the pi electrons of the ring and increase the electron density of the ring. This in turn would tend to promote dimer formation relative to the porphyrin systems.

#### B. Ligand Binding Properties

Several ligands (see experimental section) were added to Ni-TSPC<sup>4-</sup> in aqueous solution to determine if any would coordinate to the axial positions of the complex. Only pyridine, bipyridine, and tripyridine ligands bind according to spectral measurements with pyridine effecting the largest spectral changes. Consequently, only this ligand was examined. In aqueous pyridine solutions of Ni-TSPC<sup>4-</sup>, a new isosbestic point at 652 nm forms indicating that an equilibrium between the ligand and Ni-TSPC<sup>4-</sup> exists. The following equilibrium is proposed,  $D + 2Py = D(Py)_2$ . The species present in the equilibrium and the equilibrium constant were obtained from spectral measurements using a modified version of the Benesi-Hildebrand equation listed below:

$$\frac{[Py]^n}{\frac{nA}{\ell C_T} - \epsilon_D} = \frac{[Py]^n}{\epsilon_{DL_2} - \epsilon_D} + \frac{1}{\beta_2(\epsilon_{DL_2} - \epsilon_D)} \quad (9)$$

$$\frac{(\epsilon_{DL_2} - \epsilon_D)}{\frac{nA}{\ell C_T} - \epsilon_D} = \frac{1}{\beta_2(\text{Py})^n} + 1 \quad (10)$$

Where [Py] = the concentration of pyridine added  
 $[\epsilon_{DL_2}]$  = molar optical absorptivity of the pyridinated dimer  
 $[\epsilon_D]$  = molar optical absorptivity of the dimer

A = absorbance of the solution at a given wavelength  
 $\ell$  = optical path length

$C_T$  = total concentration of Ni-TSPC<sup>4-</sup>

$\beta_2$  = overall equilibrium constant

n = number of pyridine molecules added to each species

A plot of  $[L^2] / \left( \frac{2A}{\ell C_T} - \epsilon_D \right)$  vs  $[L]^2$  where L = Py yields a straight line with a slope of  $\frac{1}{\epsilon_{DL_2} - \epsilon_D}$  and an intercept of  $\frac{1}{(\beta_2)(\epsilon_{DL_2} - \epsilon_D)}$ . Using a  $5 \times 10^{-6}$  M Ni-TSPC<sup>4-</sup> solution

over a pyridine concentration range of 2-6% (by volume),  $\epsilon_{DL_2}$  was found to be  $2.88 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$  (see Figure 6). From equation (10), a plot of  $(\epsilon_{DL_2} - \epsilon_D) / \left( \frac{2A}{\ell C_T} - \epsilon_D \right)$  vs  $1/[L]^2$  yields a straight line with a slope of  $(1/\beta_2)$  from which the overall equilibrium constant is obtained (see Figure 7). Equilibrium constants obtained with different concentrations of Ni-TSPC<sup>4-</sup> and pyridine were in excellent agreement. Their values at 15°, 21°, 30°, 35° and 40°C were 1.7, 1.9, 2.8, 3.6, and  $4.4 \text{ M}^{-2}$ , respectively. It has been reported that the linearity of the above-mentioned plots is a test for the proposed equilibrium.<sup>44</sup> Only when n = 2 are linear plots obtained from equation (9) and equation (10)

Figure 6. Plot of  $[L]^2 / \left( \frac{2A}{\ell C_T} - \epsilon_D \right)$  vs  $[L]^2$  for the  
Determination of  $\epsilon_{DL_2}$ .



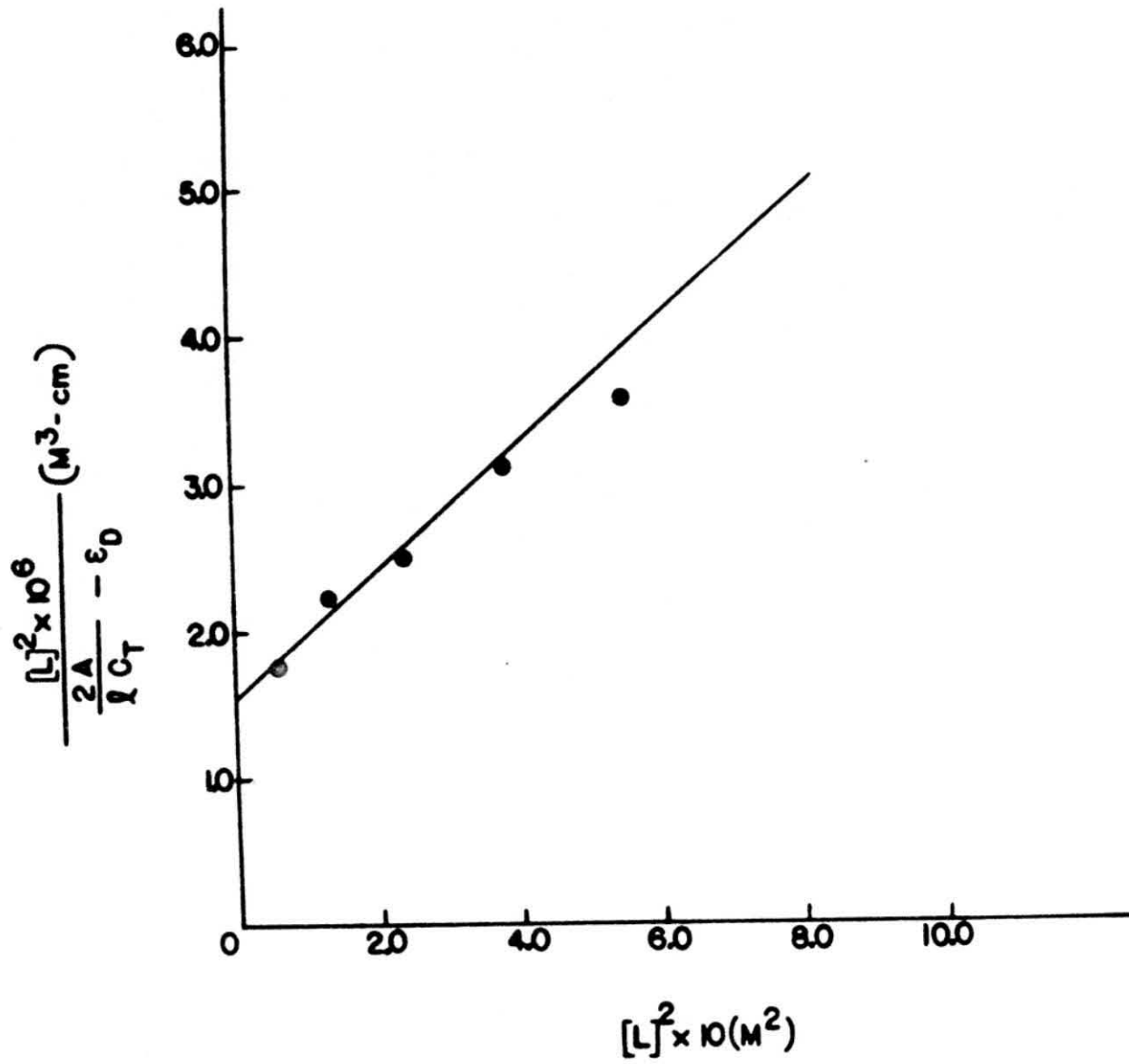
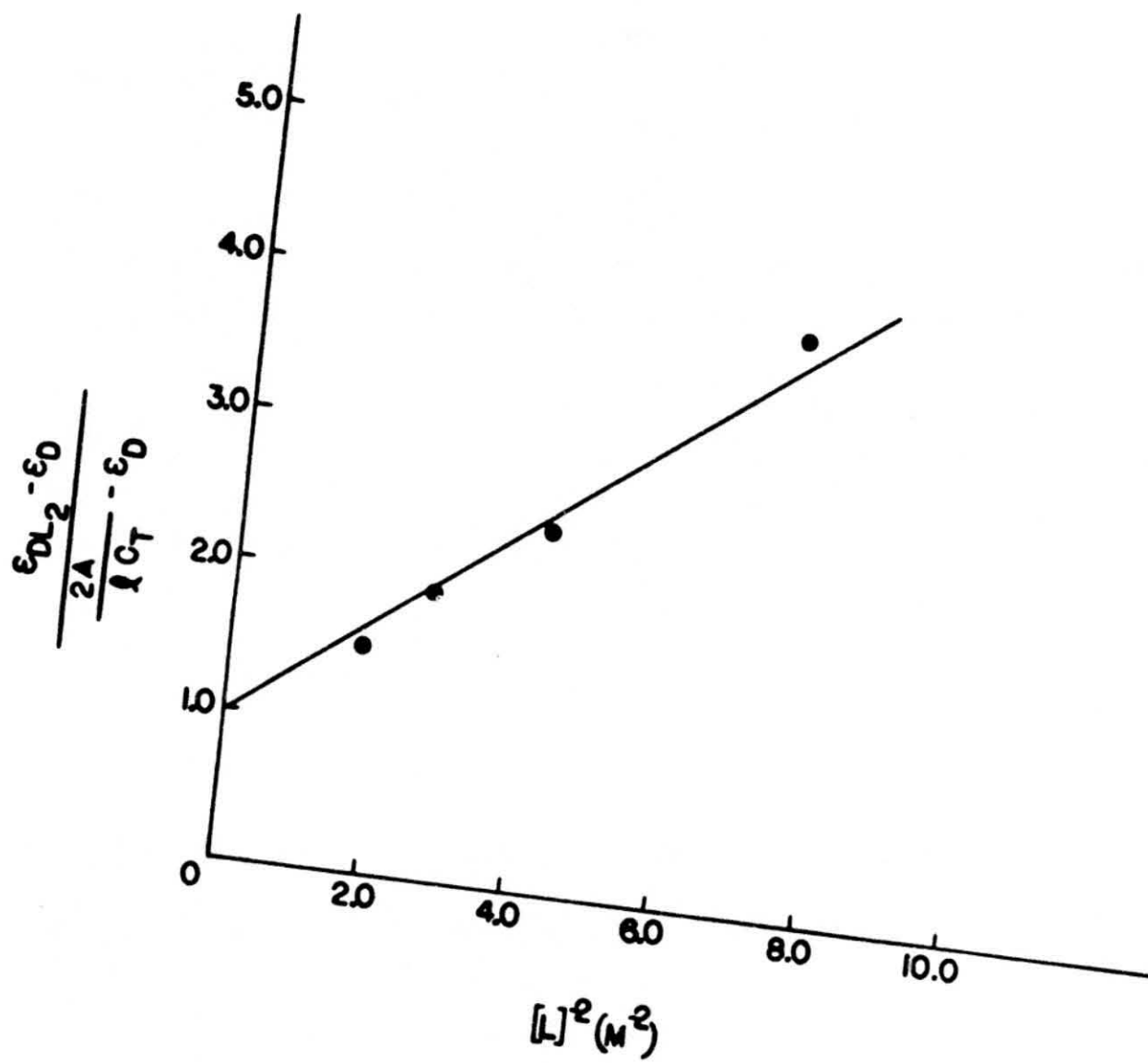


Figure 7. Plot of  $(\epsilon_{DL_2} - \epsilon_D) / \left(\frac{2A}{\ell C_T} - \epsilon_D\right)$  vs  $1/[L]^2$   
for the Determination of  $\beta_2$ .



while nonlinear plots were obtained for other proposed equilibrium. The addition of pyridine to the dimer instead of the monomer is consistent with the positions of the spectral bands and the spectral shifts reported in the literature for other analogous systems.<sup>44,45,48</sup> One band is located at the same wavelength as the dimer in aqueous solution while the second band is shifted to the same extent exhibited in porphyrin systems. In the Ni-TSPC(Py)<sub>2</sub><sup>4-</sup> system, the shift of the new band from the dimer position is about 40 nm.

The addition of pyridine to the dimer instead of the monomer is supported by the observation that no spectral change occurs upon addition of pyridine to Ni-TSPC<sup>4-</sup> in DMSO where only the monomer is present.<sup>4,20</sup> One possible explanation for the addition of pyridine to the dimer instead of the monomer is that a greater transfer of electron density from the central metal to the phthalocyanine ring occurs in the dimer which would enhance the pi-pi interaction of the monomer units and stabilize the dimer. Moreover, the decrease of electron density on the central metal would promote ligand binding to its open axial position.

The increase of  $\beta_2$  with temperature shows that the addition of pyridine to Ni-TSPC<sup>4-</sup> is an endothermic process. The Gibbs-Helmholtz plot yields a  $\Delta H^\circ$  value of 6.9 kcal/mole. Despite the unfavorable enthalpy change, the addition of pyridine is thermodynamically favorable ( $\Delta G^\circ = -.62$  kcal/mole at 30°C) due to the entropy change ( $\Delta S^\circ = 25$  e.u.). Table 7 presents the thermodynamic parameters for this system.

Table 7

Thermodynamic Parameters of the Ni-TSPC(Py)<sub>2</sub><sup>4-</sup> System

Temp (°C)	$\beta_2$ (M <sup>-2</sup> )	$\Delta G^\circ$ (kcal/mole)	$\Delta H^\circ$ (kcal/mole)	$\Delta S^\circ$ (e.u.)
15	1.7	-.30	6.9	25
21	1.9	-.38	6.9	25
30	2.8	-.62	6.9	25
35	3.6	-.78	6.9	25
40	4.4	-.92	6.9	25

Due to the lack of information on pyridine - metallo-phthalocyanine systems, a comparison of equilibrium constants with other  $M\text{-TSPC}^{4-}$  is not possible. In fact, a comparison of  $\text{Ni-TSPC(Py)}_2^{4-}$  with Nickel(II) porphyrin systems (see Table 8) is also not feasible because of the effect of different solvents on the stability of the pyridinated species as well as the different number of pyridine molecules complexed.

Table 8

Equilibrium Constants of Some Pyridinated Ni(II)-Porphyrins  
and the Ni-TSPC<sup>4-</sup> Complex

Complex	$K_s$	T (°C)	Solvent	Ref.
Ni(II)-tetraphenylporphine(Py)	.05	30	Benzene	48
Ni(II)-mesotetraphenylporphine(Py)	1016	25	Chloroform	49
Ni(II)-tetrapyriddyloporphine(Py) <sub>2</sub>	501	25	Chloroform	50
Ni(II)-hematoporphine(Py) <sub>2</sub>	32	25	Chloroform	50
Ni(II)-TSPC(Py) <sub>2</sub>	2.80	30	Water	this work

## RECOMMENDATIONS

Some possible recommendations for future studies with Ni-TSPC<sup>4-</sup> and other substituted and unsubstituted metallophthalocyanines are as follows:

1. For additional spectral studies of Ni-TSPC<sup>4-</sup> in blood serum, it is recommended that the blood serum be filtered to a constant protein level prior to use.
2. Kinetic measurements on the addition of pyridine to Ni-TSPC<sup>4-</sup> should be made using concentration-jump relaxation methods.
3. Spectral studies could be made on the second and third row transition metals to examine the effect of metallic size on the polymerization properties of tetrasulfonated metallophthalocyanine complexes.
4. The effect of different solvents on the Ni-TSPC<sup>4-</sup> monomer-dimer equilibrium should be examined.
5. A spectral examination could be made on the influence of different ring substituents on the monomer-dimer equilibrium of the Ni-TSPC<sup>4-</sup> complex.
6. The effects of bipyridine and tripyridine on the monomer-dimer equilibrium of Ni-TSPC<sup>4-</sup> should be examined.
7. A study of the oxygen uptake properties of Ni-TSPC<sup>4-</sup> in other solvents should be made.



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