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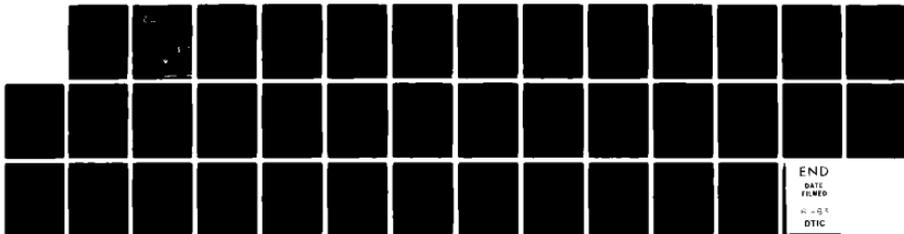
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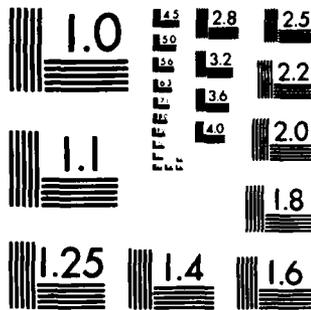
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US Army Armament Research and Development Command
Aberdeen Proving Ground, Maryland 21010

**TECHNICAL REPORT
ARCSL-TR-82088**

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**SIMULTANEOUS DETERMINATION OF
MOLAR ABSORPTION COEFFICIENTS AND EQUILIBRIUM
CONSTANTS FOR MONOMER-DIMER EQUILIBRIA**

By

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Chemical Branch
Research Division

April 1983

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20. ABSTRACT (continued)

measured for a series of dye concentrations. A nonlinear least-squares program then finds the best-fit monomer and dimer molar absorption coefficients. Absorbances are remeasured at various temperatures or with different dye concentrations and the calculation repeated. The mean molar absorption coefficients are computed from all the measurements; these values are then used to compute the dimerization constants at each temperature.

This technique was applied with cobalt (II) tetrasulfonated phthalocyanine as the dyestuff. At 662 nm the molar absorption coefficients for monomer and dimer were $9.6 \pm 0.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $7.5 \pm 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The error is the sample standard deviation of four dye solutions for measurements made at 5° over the range 15° to 45°C . This monomer value compares favorably with a value of $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ measured in a $2 \times 10^{-7} \text{ M}$ aqueous-ethanol solution for which Beer's law was obeyed.

PREFACE

The work described in this report was authorized under Project 1L161101A71A, Research in Defense Systems, Scientific Area B, Chemical Defense Research. This work was performed at CSL as part of a joint research program between BRL and CSL. The work covered in this report was performed during FY 82.

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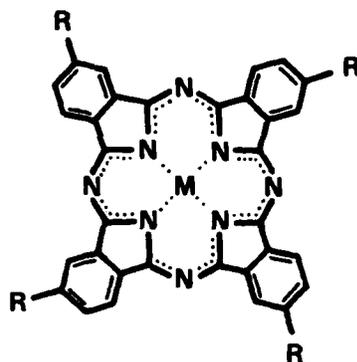
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SIMULTANEOUS DETERMINATION OF MOLAR ABSORPTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS FOR MONOMER-DIMER EQUILIBRIA

1. INTRODUCTION

Metal complexes of tetrasulfonated phthalocyanine (TSPC, figure 1), like other water-soluble dyestuffs, aggregate in aqueous solution.¹ The formation of the dimer has been the subject of repeated studies for a variety of transition-metal complexes with TSPC.²⁻⁸



R = SO₃Na (TSPC)

M = Co⁺⁺; Cu⁺⁺

Figure 1. Structure of Metal Phthalocyanines

The equilibrium constant for formation of a dimer is conveniently obtained spectrophotometrically since TSPC complexes absorb strongly in the visible region. All of the methods employed in the past to determine the dimerization constant of TSPC complexes spectrophotometrically required that the spectrum of the pure monomer be known. This spectrum is obtained by successive dilution of a dye solution until Beer's Law behavior is obeyed. In practice, there is a limit where the absorbance of the solution is too small to measure precisely. Frequently, the dye is diluted in alcoholic-aqueous solution to foster monomer formation. In addition, further approximations on the nature of the dimer spectrum are made,⁹ or the absorbance is measured with large amounts of monomer in solution to facilitate mathematical approximations.⁴ In the latter case, Reynolds and Kolstad³ contend that as much as 80% uncertainty can be introduced in the value of the dimerization constant.

This report describes results for a more general scheme that we devised based on a method introduced by Monahan in 1970¹⁰ in which a nonlinear least-squares program computes best-fit molar absorbance coefficients for both monomer and dimer simultaneously from absorbance measurements over a range of dye concentrations. The method is illustrated with cobalt (II) tetrasulfonated phthalocyanine (CoTSPC) as the dyestuff.

2. MATERIAL AND METHODS

2.1 Preparation of [29H,31H-phthalocyanine-2,9,16,23-tetrasulfonato(2-)- N²⁹,N³⁰,N³¹,N³²] Cobalt (CoTSPC).

This material was prepared by the method of Weber and Busch¹¹ using the sodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate, and cobalt sulfate heptahydrate in hot nitrobenzene. The purification procedure for this 0.05-mol scale reaction differed slightly from the published method. The crude, dark-blue product was broken apart with a spatula, rinsed with 400 ml methanol, and was finely ground in a mortar. The resulting blue powder was dissolved in 1.1 l of 1N HCl saturated with sodium chloride to give a deep blue slurry that was heated to reflux briefly, then was cooled to room temperature and filtered. The air-dried product was dissolved in 700 ml of 0.1N sodium hydroxide, heated to 80°C and filtered (no residue). Sodium chloride (270 gm) was added to salt out the product. This slurry was heated with stirring at 80°C for 3 hours while ammonia evolved. Upon cooling to room temperature, the product was isolated by filtration. This reprecipitation was repeated twice and the final precipitate was washed with 1.8 l of 80% aqueous ethanol to remove occluded NaCl. A convenient final purification was achieved by washing the blue powder in the thimble of a Soxhlet apparatus with hot 95% ethanol for 18 hours. The product was then dried *in vacuo* for 2 days to give 22.0 gm (54%) of the desired CoTSPC as determined by UV-VIS spectroscopy.

2.2 Spectrophotometric Measurements.

All spectrophotometric measurements are made with a Beckman Model 25 UV-VIS Spectrophotometer using a cell with a 1-cm path length. The CoTSPC solutions were equilibrated for at least 30 minutes in a water bath that was also connected to the cell compartment of the instrument. The solution was transferred to the spectrophotometer cell and allowed another 3 to 5 minutes to equilibrate. The temperature of the solution was recorded with the thermocouple in the cell compartment that is integral to the spectrophotometer. This thermocouple was calibrated against an NBS thermometer. The water bath kept the cell compartment temperature within $\pm 0.1^\circ\text{C}$.

2.3 Determination of Molar Absorption Coefficients.

The absorbance of a solution in a 1-cm cell containing only monomer and dimer is

$$A = \epsilon_M [M] + \epsilon_D [D] \quad (1)$$

where

A = absorbance

ϵ_M = molar absorption coefficient, monomer, $\text{M}^{-1}\text{cm}^{-1}$

ϵ_D = molar absorption coefficient, dimer, $\text{M}^{-1}\text{cm}^{-1}$

[M] = monomer concentration, M

[D] = dimer concentration, M.

The equilibrium between monomer and dimer is

$$K = \frac{[D]}{[M]^2} \quad (2)$$

where K = dimerization constant, M^{-1} .

The total concentration of CoTSPC ($[Co]$) is

$$[Co] = [M] + 2 [D] \quad (3)$$

Equations 2 and 3 can be combined to give the monomer concentration in terms of total CoTSPC as

$$[M] = \frac{-1 + \sqrt{1 + 8K [Co]}}{4K} \quad (4)$$

With equations (2) and (4), one can rewrite equation (1) in terms of the experimentally accessible total concentration of CoTSPC as

$$A = \epsilon_M \left(\frac{-1 + \sqrt{1 + 8K [Co]}}{4K} \right) + \frac{\epsilon_D}{2} \left[[Co] - \left(\frac{-1 + \sqrt{1 + 8K [Co]}}{4K} \right) \right] \quad (5)$$

A series of solutions with different CoTSPC concentrations was made from aliquots of four stock solutions of CoTSPC. The absorbances of these solutions were measured at a given wavelength after temperature equilibration. A nonlinear least-squares program¹² based on the Gauss-Newton technique was used to fit the measured absorbances versus CoTSPC concentrations to equation 5. The program found best-fit values of ϵ_M , ϵ_D , and K and also recalculated the absorbances with these best-fit values. The absorbance measurements were then made at different temperatures. Mean values of the best-fit ϵ_M and ϵ_D were determined from all the experiments. These values were fixed and equation 5 was used to find best-fit values of K for each stock solution and temperature.

The monomer's molar absorption coefficient was also measured by diluting CoTSPC in 20% (by volume) ethanol-water solutions until Beer's Law behavior was observed. Equation 5 will approach

$$A = \epsilon_M [Co] \quad (6)$$

where $8K[Co] \ll 1$, since $(1 + 2x)^{\frac{1}{2}} \approx (1 + x)$, when $2x \ll 1$.

3. RESULTS AND DISCUSSION

3.1 CoTSPC Spectrum in Water.

Figure 2 illustrates spectra of a $1.17 \times 10^{-5} M$ solution of CoTSPC between 600 and 700 nm that was heated to 70°C and allowed to cool to room temperature. The shoulder near 620 nm grew and the peak near 660 nm decreased as more dimer formed at the lower temperature. The presence of the isosbestic point at 634 nm

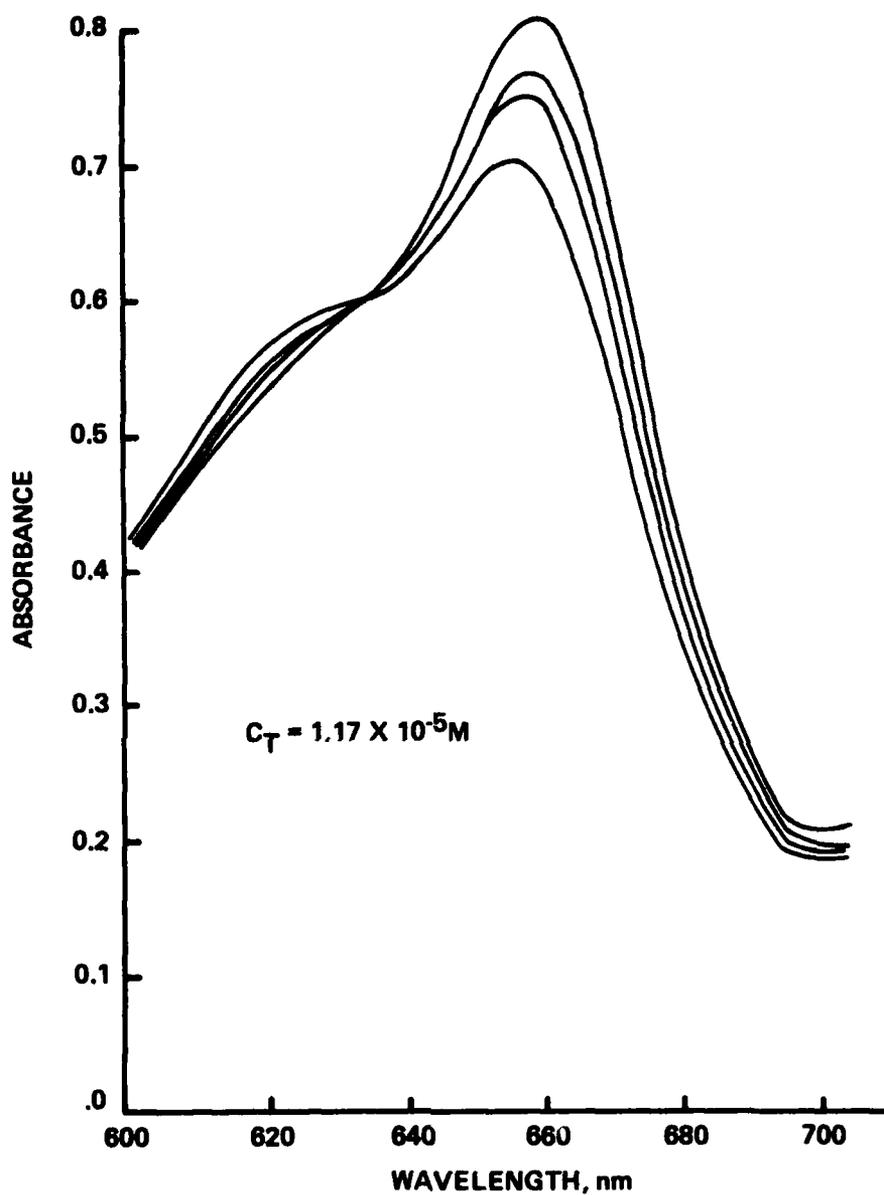


Figure 2. Decrease in Absorbance at 662 nm of CoTSPC and Formation of Isosbestic Point at 634 nm on Cooling to Room Temperature from 70°C

was taken as evidence that only monomer and dimer existed at this concentration. To avoid interference from higher aggregates, subsequent stock solutions were made no more concentrated than $1.2 \times 10^{-5}M$.

3.2 Monomer Spectrum by Dilution in Ethanol-Water.

In order to estimate a molar absorption coefficient for the pure monomer, 1-ml aliquots of a stock solution were diluted to volume with a 20% by volume ethanol-water solution in a series of volumetric flasks. The shoulder near 620 nm disappeared and one nearly symmetrical peak centered at 662 nm remained as the solutions were diluted. Table 1 lists the absorbances recorded at the peak heights along with the corresponding molar absorption coefficients. Since it was necessary to use the 0.1 absorbance full-scale setting, the absorbances for the 25-, 50-, and 100-ml dilutions were remeasured to test the reproducibility of the instrument. These results are also listed in table 1.

Table 1. Maximum Absorbances for CoTSPC Diluted with 20% by Volume Ethanol-Water*

Dilution	[CoTSPC] M ($\times 10^7$)	A	ϵ $M^{-1}cm^{-1}$ ($\times 10^{-5}$)	A**	ϵ $M^{-1}cm^{-1}$ ($\times 10^{-5}$)
1:10	11.5	0.112	0.98	—	—
1:25	4.60	0.0472	1.03	0.0479	1.05
1:50	2.30	0.0242	1.06	0.0243	1.06
1:100	1.15	0.0113	0.99	0.0117	1.02
1:250	0.46	0.0041	0.92	—	—

* 1 cm cell; $\lambda = 662$ nm

** Measured absorbance for second trial with same solution.

One can see that the molar absorption coefficient is constant for a $2 \times 10^{-7}M$ solution within the precision of the experiment. Table 2 lists results for a series of solutions prepared from 1-ml aliquots of stock solutions diluted with the ethanolic-water solution into a 50-ml volumetric flask. The mean molar absorption coefficient at 662 nm is $1.05 \pm 0.02 \times 10^5 M^{-1}cm^{-1}$, the error expressed as the sample standard deviation for the eight solutions. Other reported values are $1.03 \times 10^5 M^{-1}cm^{-1}$ at $\lambda = 663$ nm,¹³ determined by heating a water solution until the absorbance was constant, and $1.2 \times 10^5 M^{-1}cm^{-1}$ at $\lambda = 663$ nm,¹⁴ determined by dilution in ethanol-water solution.

Table 2. Molar Absorption Coefficients of Monomeric CoTSPC in 20% by Volume Ethanol-Water*

[CoTSPC] M x 10 ⁷	A	ϵ M ⁻¹ cm ⁻¹ (x 10 ⁻⁵)
2.30	0.0242	1.06
2.34	0.0244	1.04
1.81	0.0186	1.03
2.49	0.0259	1.04
1.58	0.0161	1.02
1.61	0.0172	1.07
2.24	0.0237	1.06
1.74	0.0181	1.05

*1 cm cell; $\lambda = 662$ nm

3.3 Simultaneous Determination of Monomer-Dimer Molar Absorption Coefficients.

The molar absorption coefficients of the monomer and dimer were determined at 662 nm corresponding to the peak absorbance for the monomer. A stock solution of CoTSPC and three aliquots of different volumes were used to prepare four solutions with different CoTSPC concentrations. The absorbances of these solutions were measured at 662 nm and the absorbances fit to equation 5 with the nonlinear least-squares program to give best-fit values of ϵ_M , ϵ_D , and K, and absorbances recalculated with these values.

Sets of solutions were prepared from four stock solutions (A, B, C, and D) and the absorbances for each set of solutions were measured over the temperature range 15° to 45°C at 5°C intervals. In order to get the calculation to converge, it was necessary to use numbers near unity, so the concentrations of CoTSPC were multiplied by 10⁵. In a few instances, negative best-fit values of ϵ_D or K were computed, or the magnitude of the standard deviation exceeded the value of ϵ_D . Where negative or near-zero values were encountered, the values of ϵ_M and ϵ_D were both discarded. Values of ϵ_D were discarded where the standard deviation exceeded the computed value.

Appendix A contains the results of these experiments. Table 3 summarizes the values of ϵ_M and ϵ_D along with the mean value and sample standard deviation for each solution over the indicated temperature range. The values of ϵ_M and ϵ_D averaged over the four solutions are $9.65 \pm 0.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $7.62 \pm 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, the error being the sample standard deviation. The value of ϵ_M compares favorably with the $1.05 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ measured

Table 3. Summary of ϵ_M and ϵ_D Computed from Least-Squares Treatment of Absorbances versus CoTSPC Concentration at 662 nm

Temperature °C	ϵ_M for solution				ϵ_D for solution			
	A	B	C	D	A	B	C	D
	$M^{-1}cm^{-1} \times 10^{-4}$				$M^{-1}cm^{-1} \times 10^{-4}$			
16.1	9.23	9.25	8.32	*	7.04	6.94	6.34	*
20.1	9.49	8.54	9.08	9.32	8.30	6.58	6.64	7.55
24.2	10.7	9.04	9.07	8.98	8.30	6.64	7.25	6.65
29.6	10.3	10.7	9.28	13.5	8.82	8.34	7.19	9.59
34.6	9.10	*	*	9.4	3.42	*	*	7.00
41.0	9.51	*	*	10.8	**	*	*	10.3
45.6	9.90	9.55	9.34	10.2	8.76	7.32	**	11.0
Mean	9.75	9.42	9.02	10.4	7.44	7.17	6.80	8.68
Sample Standard Deviation	0.6	0.8	0.4	1.7	2.1	0.9	0.5	1.8

* Negative value of ϵ_M , ϵ_D , or K

** Standard deviation exceeds value

in the dilute ethanolic-aqueous solution, considering the associated errors. Monahan also reported a similar error in his determinations.¹⁰

In order to obtain dimerization constants, the absorbance versus concentration data were refit to equation 5 using fixed values of ϵ_M and ϵ_D . The best fit dimerization constants and absorbances calculated with them are listed in appendix B. The difference between the calculated and experimental absorbances is generally within experimental error. Table 4 summarizes the dimerization constants determined with fixed values of ϵ_M and ϵ_D .

As a further check on the self-consistency of this method for determining dimerization constants, a set of absorbances was then measured for new solutions which had not been used to compute the values of ϵ_M and ϵ_D . Appendix C summarizes the results of these experiments. Table 5 lists the values as K', the dimerization constants for solutions independent of the determination of ϵ_M and ϵ_D . Table 6 compares the values of K and K' at the various temperatures.

Table 4. Summary of Dimerization Constants Determined with ϵ_M and ϵ_D Fixed*

Temperature	K of Solution				Mean	Sample Standard Deviation
	A	B	C	D		
°C	$M^{-1} \times 10^{-5}$					
16.1	4.04	4.42	4.29	4.93	4.17	0.22
20.1	2.75	3.22	3.11	2.99	3.02	0.20
24.2	2.23	3.51	2.45	2.34	2.38	0.12
29.6	1.70	1.78	1.83	1.76	1.77	0.05
34.6	1.12	1.23	1.22	1.18	1.19	0.05
41.0	0.758	0.829	0.856	0.815	0.814	0.04
45.6	0.572	0.639	0.604	0.565	0.595	0.03

* $\epsilon_M = 9.65 \times 10^4 M^{-1} cm^{-1}$; $\epsilon_D = 7.52 \times 10^4 M^{-1} cm^{-1}$ at $\lambda = 662 nm$

Table 5. Summary of Dimerization Constants with Solutions* Which Were not Used for Determining ϵ_M and ϵ_D

Temperature	K' of Solution				Mean	Sample Standard Deviation
	A	B	C	D		
°C	$M^{-1} \times 10^{-5}$					
20.1	3.21	2.97	2.95	3.09	3.06	0.12
24.9	2.19	2.13	2.00	2.07	2.10	0.08
29.6	1.77	1.59	1.58	1.64	1.64	0.09
34.2	1.28	1.19	1.10	1.20	1.19	0.07
41.0	0.803	0.754	0.710	0.716	0.746	0.04

* $\epsilon_M = 9.65 \times 10^4 M^{-1} cm^{-1}$; $\epsilon_D = 7.52 \times 10^4 M^{-1} cm^{-1}$ at $\lambda = 662 nm$

Table 6. Comparison of Mean Dimerization Constants*

Temperature °C	K M ⁻¹ x 10 ^{-5**}	K' M ⁻¹ x 10 ⁻⁵
16.1	4.17 ± 0.22	-
20.1	3.02 ± 0.20	3.06 ± 0.12
24.2	2.38 ± 0.12	-
24.9	-	2.1 ± 0.08
29.6	177 ± 0.05	1.64 ± 0.09
34.2	-	1.19 ± 0.07
34.6	1.19 ± 0.05	-
41.0	0.814 ± 0.04	0.746 ± 0.04
45.6	0.595 ± 0.03	-

* Error expressed as sample standard deviation.

** Determined with solutions used to establish values for molar absorption coefficients.

Since the dimerization constants were measured in dilute CoTSPC solutions (10⁻⁵ to 10⁻⁶M), one can assume that these dimerization constants represent the thermodynamic equilibrium constants from which the standard-state free energy, ΔF° , can be determined through the familiar expression

$$\Delta F^\circ = -RT \ln(K) \quad (7)$$

The temperature dependence of ΔF° can then be used to determine the standard-state enthalpy and entropy of dimerization.

Figure 3 illustrates a plot of $\ln(K)$ versus $1/T$ suggesting that the enthalpy is independent of temperature. Values of ΔH° and ΔS° were then determined with the nonlinear, least-squares program by fitting the data in table 6 to

$$K = e \left(-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \right) \quad (8)$$

The best-fit values of ΔH° and ΔS° are 12.0 ± 0.03 kcal/mole and -16 ± 1 cal/mole-K, respectively, with the error expressed as the standard deviation of the mean, an output of the program.¹² Table 7 compares dimerization constants calculated with the best-fit values of ΔH° and ΔS° with the experimental values.

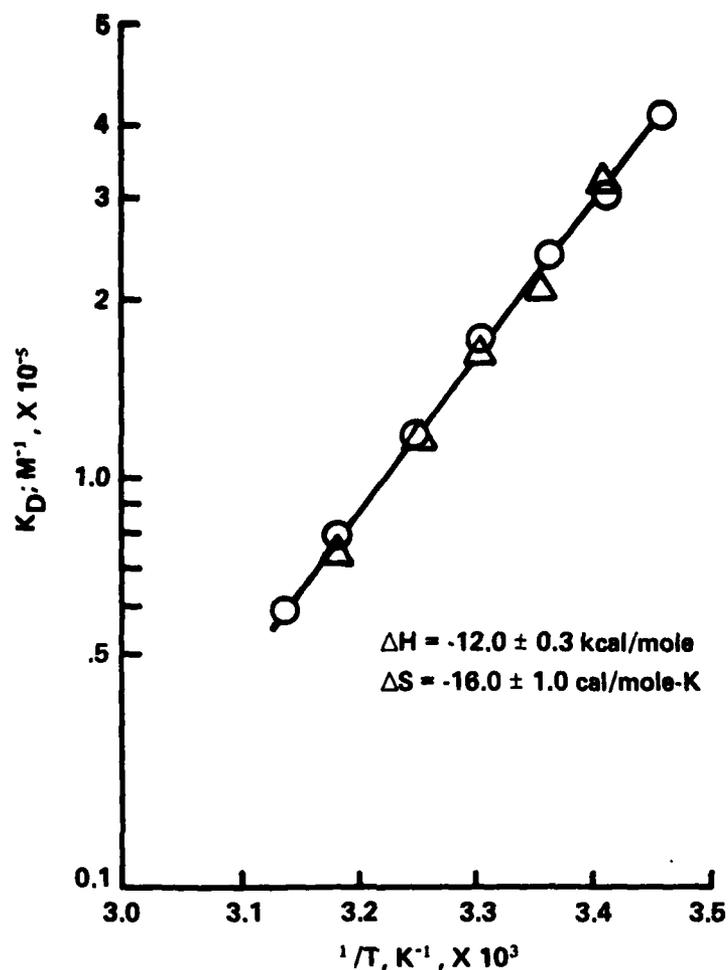


Figure 3. Temperature Dependence of the Dimerization Constant of CoTSPC in Water; (Δ) Data Points Represent K'_0

Recently, Blandamer and co-workers¹⁵ have questioned the physical significance of the values obtained from least-squares treatment of the temperature dependence of rate or equilibrium data, particularly when the parameters being fit have unit correlation coefficients, as is the case here. These workers propose the following expression¹⁶ for determining activation parameters as well as checking the temperature dependence of ΔH° :

$$K = K_0 e^{\left\{ \frac{\Delta H_0^\circ}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta C_p^\circ}{R} \left(\ln \frac{T}{T_0} + \frac{T_0}{T} + 1 \right) \right\}} \quad (9)$$

where

- K = equilibrium constant at T
- K_0 = equilibrium constant at T_0
- ΔC_p° = standard heat capacity.

Table 7. Comparison Between Experimental Dimerization Constant and Those Calculated with Best-Fit Activation Parameters*

Temperature °C	K Experiment $M^{-1} \times 10^{-5}$	K Fit $M^{-1} \times 10^{-5}$
16.1	4.17	4.13
20.1	3.02; 3.06	3.10
24.2	2.38	2.33
24.9	2.10	2.22
29.6	1.77; 1.64	1.62
34.2	1.19	1.20
34.6	1.19	1.17
41.0	0.814; 0.746	0.784
45.6	0.595	0.593

* $\Delta H^\circ = -12.0 \pm 0.3$ kcal/mole; $\Delta S^\circ = -16 \pm 1$ cal/mole - K.

This equation is obtained from integration of the van't Hoff isochore between T_0 and T which assumes ΔC_p° is independent of temperature. The quantities K and K_0 are the equilibrium constants at T and T_0 , respectively, and ΔH_0° is the enthalpy at T_0 . For a set of K , T data, any pair are selected as K_0 and T_0 , and the remaining values fit to equation 9 to find best-fit values of ΔH_0° at T_0 and ΔC_p° . The calculation is repeated with new values of K_0 , T_0 until values of ΔH_0° and ΔC_p° have been obtained for each value of T in the data set.

The non-linear least-squares program was modified for fitting the K , T data in table 6 to equation 9, in which ΔH_0° and ΔC_p° were parameters to be fit while K_0 and T_0 were inserted as fixed parameters. Table 8 summarizes the results of determinations of ΔH° and ΔC_p° at each of the nine temperatures from table 6. One sees that the enthalpy is independent of temperature, and the mean value of ΔH° , -12.0 ± 0.6 kcal/mole (error representing sample standard deviation), is identical to the value of -12.0 ± 0.3 kcal/mole obtained from fitting the K , T data to equation 8.

Finally, table 9 lists the results Eyring⁷ obtained for the thermodynamics of CoTSPC dimerization from kinetic and spectrophotometric methods at 38°, 48°, and 58°C. The agreement with the thermodynamic parameters measured kinetically is gratifying.

Table 8. Results of Calculations to Determine ΔH° Using Equation 9

Temp °C	ΔH° kcal/mole	ΔC_p° cal/mole-K
16.1	-12.4 \pm 0.6	28 \pm 68*
20.1	-11.2 \pm 0.8	54 \pm 95
24.2	-11.1 \pm 0.7	-156 \pm 117
24.9	-12.3 \pm 1.0	154 \pm 151
29.6	-11.4 \pm 0.5	-230 \pm 118
34.2	-12.2 \pm 0.7	- 39 \pm 117
34.6	-12.0 \pm 0.7	- 63 \pm 108
40.1	-12.7 \pm 0.8	- 80 \pm 87
45.6	-12.6 \pm 0.7	- 53 \pm 62

*Error represents standard deviation of the mean.

Table 9. Thermodynamic Parameters for CoTSPC Dimerization in Water

ΔH° kcal/mole	ΔS° cal/mole-K	Method	Reference
-12.6 \pm 1.3*	-14 \pm 4*	Ratio of rate coefficients	7
-14 \pm 0.9*	-18 \pm 3*	Spectrophotometric	7
-12.3 \pm 0.3**	-16 \pm 1**	Spectrophotometric	This work

* Error estimated by authors.

** Standard deviation of the mean.

These results suggest that this technique would be particularly useful in the study of other dye aggregation phenomena, such as the copper phthalocyanine system, where the pure monomer spectrum can not be obtained. We also plan to use this technique to determine the effect of hydroxylic solvents on phthalocyanine aggregation.

4. CONCLUSIONS

a. A spectrophotometric method that does not require the monomer spectrum to be known in advance has been devised for measuring the equilibrium between monomer and dimer.

b. The method was illustrated using cobalt (II) tetrasulfonated phthalocyanine, for which the dimerization constant was measured at 5° intervals over the temperature range 15° to 45°C. It was shown that the enthalpy of reaction is independent of temperature over this range, being -12.0 ± 0.3 kcal/mole with corresponding entropy of -16 ± 1 cal/mole K.

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APPENDIX A

ABSORBANCE MEASUREMENTS AT 662 nm TO DETERMINE ϵ_M AND ϵ_D

Table A-1. Determination of ϵ_M and ϵ_D for Solution A

[CoTSPC], M x 10 ⁶	Temperature														
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C		
	A _e ^a	A _f ^b	A _e	A _f	A _e	A _f									
8.09	0.457	0.457	0.485	0.485	0.498	0.498	0.519	0.519	0.519	0.549	0.549	0.579	0.579	0.498	0.498
4.04	0.253	0.253	0.265	0.265	0.274	0.274	0.284	0.284	0.306	0.306	0.324	0.324	0.329	0.329	0.329
2.02	0.140	0.140	0.144	0.145	0.152	0.152	0.156	0.156	0.164	0.165	0.173	0.174	0.175	0.175	0.176
0.809	0.063	0.063	0.065	0.065	0.069	0.069	0.070	0.070	0.071	0.070	0.075	0.074	0.076	0.076	0.075
$\epsilon_M, M^{-1}cm^{-1} \times 10^{-5}$	-	0.923	-	0.949	-	1.07	-	1.03	-	0.910	-	0.951	-	0.990	-
$\epsilon_D, M^{-1}cm^{-1} \times 10^{-5}$	-	0.704	-	0.830	-	0.830	-	0.882	-	0.842	-	0.142 ^c	-	0.876	-
K, M ⁻¹ x 10 ⁻⁵	-	2.77	3.39	3.39	-	4.56	-	3.57	-	0.410	-	0.309	-	0.858	-

a Experimental absorbance

b Absorbance calculated with best-fit values

c Standard deviation exceeds value

Table A-2. Determination of ϵ_M and ϵ_D for Solution B

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.9°C		34.9°C		41.0°C		45.0°C	
	A_e^a	A_f^b	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f
1.07	0.490	0.490	0.521	0.521	0.539	0.539	0.567	0.567	0.597	0.597	0.632	0.632	0.632	0.650
4.54	0.276	0.276	0.290	0.290	0.300	0.300	0.315	0.313	0.335	0.335	0.335	0.354	0.360	0.360
2.27	0.154	0.153	0.156	0.150	0.165	0.165	0.170	0.173	0.178	0.179	0.184	0.185	0.183	0.183
0.907	0.060	0.060	0.070	0.071	0.073	0.073	0.080	0.078	0.076	0.075	0.079	0.077	0.082	0.082
$\epsilon_M^{-1} \text{ cm}^{-1} \times 10^{-5}$	-	0.925	-	0.854	-	0.904	-	1.07	-	0.853	-	0.856	-	0.955
$\epsilon_D^{-1} \text{ cm}^{-1} \times 10^{-5}$	-	0.694	-	0.685	-	0.664	-	0.834	-	-0.415 ^c	-	7.00 ^c	-	0.752
K, M ⁻¹ x 10 ⁻⁵	-	2.94	-	1.24	-	1.42	-	3.72	-	0.152	-	-0.020	-	0.976

a Experimental absorbance

b Absorbance calculated with best-fit values

c Standard deviation exceeds value

Table A-3. Determination of ϵ_M and ϵ_D for Solution C

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.01°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f	A _e	A _f	A _e	A _f						
9.66	0.528	0.528	0.551	0.551	0.572	0.572	0.596	0.596	0.630	0.630	0.665	0.665	0.698	0.698
4.83	0.294	0.293	0.309	0.307	0.317	0.316	0.330	0.330	0.355	0.354	0.370	0.369	0.387	0.386
2.42	0.161	0.162	0.167	0.170	0.172	0.173	0.181	0.181	0.190	0.192	0.196	0.197	0.206	0.207
0.966	0.072	0.071	0.078	0.076	0.078	0.077	0.080	0.080	0.083	0.081	0.084	0.082	0.088	0.087
$\epsilon_M, M^{-1}cm^{-1} \times 10^{-5}$	-	0.832	-	0.908	-	0.907	-	0.928	-	0.879	-	0.882	-	0.934
$\epsilon_D, M^{-1}cm^{-1} \times 10^{-5}$	-	0.634	-	0.664	-	0.725	-	0.719	-	0.683 ^c	-	0.016 ^c	-	0.197 ^c
K, M ⁻¹ x 10 ⁻⁵	-	1.35	-	1.77	-	1.68	-	1.38	-	0.263	-	0.163	-	0.234

a Experimental absorbance

b Absorbance calculated with best-fit values

c Standard deviation exceeded value

Table A-4. Determination of ϵ_M and ϵ_D for Solution D

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f	A _e	A _f	A _e	A _f	A _e	A _f	A _e	A _f	A _e	A _f
5.78	0.341	0.341	0.358	0.358	0.370	0.371	0.387	0.387	0.410	0.410	0.431	0.432	0.454	0.453
4.33	0.274	0.271	0.280	0.280	0.293	0.290	0.302	0.301	0.319	0.320	0.337	0.335	0.347	0.349
2.89	0.188	0.192	0.197	0.197	0.202	0.205	0.212	0.213	0.225	0.224	0.232	0.234	0.245	0.243
1.44	0.104	0.102	0.108	0.108	0.112	0.111	0.118	0.118	0.120	0.120	0.127	0.126	0.128	0.129
$\epsilon_M, M^{-1}cm^{-1} \times 10^{-5}$	-	0.754	-	0.932	-	0.898	-	1.35	-	0.940	-	1.06	-	1.02
$\epsilon_D, M^{-1}cm^{-1} \times 10^{-5}$	-	-1.55 ^c	-	0.755	-	0.665	-	0.959	-	0.700	-	1.03	-	1.10
K, M ⁻¹ x 10 ⁻⁵	-	0.115	-	2.55	-	1.31	-	14.7 ^c	-	0.913	-	2.94	-	1.00

- a Experimental absorbance
- b Absorbance calculated with best-fit values
- c Standard deviation exceeds value

APPENDIX B

DIMERIZATION CONSTANTS DETERMINED WITH
FIXED MOLAR ABSORPTION COEFFICIENTS

Table B-1. Determination of Best-Fit K with ϵ_M and ϵ_D Fixed - Solution A

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f										
8.09	0.457	0.458	0.485	0.483	0.498	0.500	0.519	0.518	0.549	0.550	0.579	0.582	0.605	0.605
4.04	0.253	0.252	0.265	0.267	0.274	0.273	0.284	0.286	0.306	0.303	0.324	0.318	0.329	0.329
2.02	0.140	0.140	0.144	0.147	0.152	0.150	0.155	0.157	0.164	0.165	0.173	0.171	0.175	0.176
0.809	0.063	0.063	0.065	0.066	0.069	0.068	0.070	0.069	0.071	0.072	0.075	0.073	0.076	0.074
K.M ⁻¹ x 10 ⁻⁵	-	4.04	-	2.75	-	2.23	-	1.70	-	1.12	-	0.758	-	0.572

a Absorbance experimental

b Absorbance calculated with best-fit K

Table B-2. Determination of Best-Fit K with ϵ_M and ϵ_D Fixed - Solution B

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f										
9.07	0.498	0.498	0.521	0.521	0.539	0.540	0.567	0.567	0.597	0.598	0.632	0.634	0.658	0.658
4.54	0.276	0.275	0.284	0.288	0.300	0.299	0.315	0.314	0.335	0.331	0.355	0.349	0.360	0.360
2.27	0.154	0.152	0.155	0.159	0.165	0.165	0.170	0.173	0.178	0.181	0.184	0.189	0.193	0.194
0.907	0.069	0.069	0.070	0.072	0.073	0.074	0.080	0.077	0.076	0.079	0.079	0.081	0.082	0.082
K, M ⁻¹ x 10 ⁻⁵	-	4.42	-	3.22	-	2.51	-	1.78	-	1.23	-	0.839	-	0.639

a Experimental absorbance

b Absorbance calculated with best-fit K

Table B-3. Determination of Best-Fit with ϵ_M and ϵ_D Fixed - Solution C

[CoTSP], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f										
9.66	0.528	0.529	0.553	0.553	0.572	0.572	0.596	0.596	0.630	0.632	0.665	0.666	0.698	0.700
4.83	0.294	0.291	0.309	0.305	0.317	0.316	0.330	0.330	0.355	0.349	0.370	0.367	0.387	0.383
2.42	0.161	0.161	0.167	0.169	0.172	0.175	0.181	0.182	0.190	0.192	0.196	0.199	0.206	0.206
0.966	0.072	0.073	0.078	0.076	0.078	0.078	0.080	0.081	0.083	0.084	0.084	0.086	0.088	0.088
K.M ⁻¹ x 10 ⁻⁵	-	4.29	-	3.11	-	2.45	-	1.83	-	1.22	-	0.856	-	0.604

a Experimental absorbance

b Absorbance calculated with best-fit K

Table B-4. Determination of Best-Fit K with ϵ_M and ϵ_D Fixed - Solution D

[CoTSPC], M x 10 ⁶	Temperature													
	16.1°C		20.1°C		24.2°C		29.6°C		34.6°C		41.0°C		45.6°C	
	A _e ^a	A _f ^b	A _e	A _f										
5.78	0.341	0.344	0.358	0.358	0.370	0.371	0.387	0.387	0.410	0.410	0.431	0.431	0.454	0.452
4.33	0.274	0.287	0.280	0.280	0.293	0.290	0.302	0.302	0.319	0.319	0.337	0.335	0.347	0.350
2.89	0.188	0.190	0.197	0.198	0.202	0.205	0.212	0.213	0.225	0.225	0.232	0.235	0.245	0.244
1.44	0.104	0.105	0.108	0.109	0.112	0.112	0.118	0.116	0.120	0.121	0.127	0.135	0.128	0.128
K, M ⁻¹ x 10 ⁻⁵	-	3.95	-	2.99	-	2.34	-	1.76	-	1.18	-	0.815	-	0.565

^a Experimental absorbance

^b Absorbance calculated with best-fit K

APPENDIX C

DIMERIZATION CONSTANTS FOR SOLUTIONS WHICH WERE NOT USED TO DETERMINE MOLAR ABSORPTION COEFFICIENTS

Table C-1. Determination of K with ϵ_M and ϵ_D Fixed - Solution A'

[CoTSPC] $M^{-1} \times 10^6$	Temperature											
	20.1°C		24.9°C		29.6°C		34.2°C		41.0°C			
	A_e^a	A_f^b	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f
11.1	0.621	0.621	0.649	0.654	0.674	0.674	0.705	0.707	0.754	0.757		
8.34	0.485	0.485	0.512	0.512	0.527	0.528	c	-	0.592	0.593		
5.56	0.344	0.343	0.369	0.362	0.376	0.374	0.394	0.392	0.423	0.418		
2.78	0.186	0.190	0.203	0.203	0.207	0.206	0.217	0.215	0.230	0.230		
$K', M^{-1} \times 10^{-5}$	-	3.21	-	2.19	-	1.77	-	1.28	-	0.803		

a Experimental absorbance

b Absorbance calculated with best-fit K'

c Not determined

Table C-2. Determination of K with ϵ_M and ϵ_D Fixed - Solution B'

	Temperature									
	20.1°C		24.9°C		29.6°C		34.2°C		41.0°C	
	A_e^a	A_f^b	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f
$[CoTSPC]M^{-1} \times 10^6$	0.454	0.453	0.477	0.475	0.497	0.496	0.517	0.517	0.551	0.552
	0.248	0.250	0.264	0.263	0.272	0.274	0.284	0.285	0.302	0.302
	0.138	0.138	0.145	0.145	0.149	0.150	0.158	0.155	0.167	0.162
$K', M^{-1} \times 10^{-5}$	-	2.97	-	2.13	-	1.59	-	1.19	-	0.754

a Experimental absorbance

b Absorbance calculated with best-fit K'

Table C-3. Determination of K with ϵ_M and ϵ_D Fixed - Solution C'

[CoTSPC] $M^{-1} \times 10^6$	Temperature											
	20.1°C		24.9°C		29.6°C		34.2°C		41.0°C			
	A_e^a	A_f^b	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f
7.75	0.462	0.461	0.487	0.487	0.504	0.504	0.533	0.532	0.567	0.566		
3.88	0.254	0.255	0.272	0.270	0.280	0.279	0.292	0.293	0.307	0.310		
1.94	0.139	0.141	0.146	0.148	0.152	0.153	0.159	0.159	0.168	0.166		
$K', M^{-1} \times 10^{-5}$	-	2.59	-	2.00	-	1.58	-	1.10	-	0.710		

a Experimental absorbance

b Absorbance calculated with best-fit K'

Appendix C

Table C-4. Determination of K with ϵ_M and ϵ_D Fixed - Solution D'

[CoTSPC] $M^{-1} \times 10^6$	Temperature											
	20.1°C		24.9°C		29.6°C		34.2°C		41.0°C			
	A_e^a	A_f^b	A_e	A_f	A_e	A_f	A_e	A_f	A_e	A_f		
5.76	0.354	0.355	0.376	0.376	0.393	0.389	0.408	0.407	0.436	0.437		
4.32	0.280	0.278	0.294	0.294	0.306	0.304	0.318	0.318	0.341	0.340		
2.88	0.195	0.196	0.209	0.208	0.213	0.215	0.223	0.224	0.239	0.237		
$K', M^{-1} \times 10^{-5}$	-	3.09	-	2.07	-	1.64	-	1.20	-	0.716		

a Experimental absorbance

b Absorbance calculated with best-fit K'

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