Molecular Associations in Nonaqueous Solvents. II. Temperature Effects on Thermodynamics of Dye–Dye Interaction in C_6H_6

Richard C. Graham, Gary H. Henderson, and Edward M. Eyring[1]
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Earl M. Woolley
Department of Chemistry, Brigham Young University, Provo, Utah 84601

The thermodynamics of dimerization of 4,4′,4′′,4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine were determined at 35°C in benzene solvent by an adiabatic calorimetric technique. Data were interpreted by two methods, each of which yielded the same values. The values for the thermodynamics of dimerization in benzene at 35°C were: $\Delta H_D° = -12 \pm 1$ kcal/mol, $\Delta G_D° = -5.6 \pm 0.8$ kcal/mol, and $\Delta S_D° = -21 \pm 3$ cal/deg mol. A value for $\Delta C_P°$ for the range 25–35°C was calculated to be -200 ± 100 cal/deg mol.

Until recently, little work has been done on the dimerization of metal(II) phthalocyanine dyes in nonaqueous solvents (*4–6*). Previously, work has been reported for the dimerization of metal(II) phthalocyanine (*1, 2, 8, 9*), for cyanine (*10, 11*), and for arylazonaphthol (*7*) dyes in aqueous solutions. In all of these studies, the aggregation constants were determined by spectrophotometry. The purpose of this paper is to expand on the spectrophotometric method of determining an equilibrium constant to include the more traditional method of calorimetry to determine not only the equilibrium constant for the aggregation but also other thermodynamic parameters.

Experimental

The solvent used in this study was previously distilled reagent grade benzene. The water content of the solvent was determined by the Karl Fischer titration to be less than 0.03 mg H_2O/ml solvent. The 4,4′,4′′,4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine (CuPc) (Figure 1), obtained from the Xerox Corp., was thrice recrystallized by a technique similar to that described by Monahan et al. (*5*).

Calorimetric titration measurements of enthalpies of dilution of CuPc in benzene were made with the Tronac 450 adiabatic calorimeter coupled with the Tronac 1040 temperature controller. The titration apparatus was modified to include a Metrohm Herisau Dosimat automatic piston buret, coupled to a precision synchronous motor for delivery of solutions to the reaction vessel (*3*). All results of our calorimetric measurements refer to 35.0° ± 0.1°C and are reported in terms of the calorie that is defined equal to 4.184 J. All solution compositions are described in terms of molar concentrations.

Results

The results of titration of 0.00963*M* solution of CuPc in benzene into 50.00 ml of pure solvent at 35.0°C are given in Table I. Two procedures were used to calculate the enthalpy of dimerization at 35.0°C from the heat of dilution data. The first method was similar to that described by Graham et al. (*4*). A one-step equilibrium was assumed as in Reaction 1:

$$\text{CuPc} + \text{CuPc} \overset{K_D}{\rightleftharpoons} (\text{CuPc})_2 \qquad (1)$$

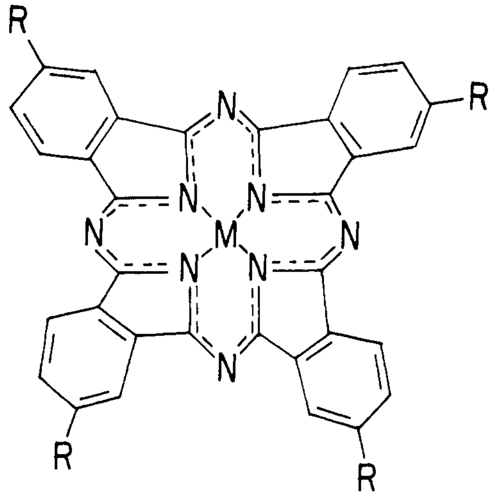

Figure 1. Monomer of 4,4′,4′′,4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine molecule where *M* denotes copper ion and *R* is $SO_2NH(CH_2)_{17}CH_3$

where $(\text{CuPc})_2$ and CuPc represent the dimer and the monomer, respectively. The following describes the procedure used to calculate $\Delta H_D°$ at 35.0°C:

(i) Calculate a K_D for the dimerization at 35°C from the van't Hoff equation and from the previously reported (*4*) *K* and $\Delta H_D°$ values at 25°.

(ii) Calculate the moles of dimer, $(\text{CuPc})_2$, in each solution of Table I by using Equations 2 and 3:

$$K_D = [(\text{CuPc})_2]/[\text{CuPc}]^2 = 8.0 \times 10^3 \qquad (2)$$

$$[\text{CuPc}] + 2\,[(\text{CuPc})_2] = (\text{ml titrant})\,(0.00963)/(50.00 + \text{ml titrant}) \qquad (3)$$

(iii) Compare pairs of resulting solutions (*k* and *l*) in Table II by using Equations 4 and 5.

$$[(\Delta H_{\text{obs}})_k - (\Delta H_{\text{obs}})_1/(\delta_k - \delta_1) = \Delta H_D° \qquad (4)$$

$$\delta = [\text{moles }(\text{CuPc})_2]/[\text{total moles CuPc}] \qquad (5)$$

(iv) Use the average value of $\Delta H_D°$ values calculated in (iii) and the previously reported (*4*) $\Delta H_D°$ value at 25°C to calculate a "better" value of K_D valid at 35° by using the van't Hoff equation.

(v) Repeat steps (ii)–(iv) as necessary to obtain agreement between $\Delta H_D°$ and K_D.

The procedure in step (iii) is used because it eliminates the necessity of inclusion in the calculations of the relatively concentrated titrant solution, since this solution may possibly contain higher polymers, $(\text{CuPc})_n$, $n \geq 3$, that would interfere with the monomer–dimer model used here (*5, 12, 13*). All measured heats of dilution are assumed to be results of reaction only, and any "nonideal" solute–solute or solute–solvent heats of interaction are assumed negligible when compared to the reaction heats (*12, 13*). Activity coefficients are assumed to be unity in all of these calculations (*12, 13*). The results of these calculations are as follows:

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[1] To whom correspondence should be addressed.

$$\Delta H_D^\circ = -11.8 \pm 0.7 \text{ kcal/mol} \tag{6}$$

$$K_D = 9.0 \pm 0.5 \times 10^3 \tag{7}$$

$$\Delta S_D^\circ = -20.2 \pm 3 \text{ cal/deg mol} \tag{8}$$

$$\Delta G_D^\circ = -5.6 \pm 0.7 \text{ kcal/mol} \tag{9}$$

Because of the larger heats of dilution at 35.0°C, another method may be used to calculate ΔH_D° and K_D simultaneously from the data (*12, 13*).

The relative apparent molar enthalpy, ϕ_L is defined as the negative of the heat of diluting a solution of specified molarity, M, to infinite dilution. Since at infinite dilution all dimers are dissociated into monomers, we may write Equation 10:

$$M\phi_L = \Delta H_D^\circ [(\text{CuPc})_2] \tag{10}$$

Equation 11 is found by combining Equation 10 with the definition of the equilibrium constant (Equation 2) and the material balance equation, $M = [\text{CuPc}] + 2[(\text{CuPc})_2]$ (*12, 13*).

$$\phi_L = \Delta H_D^\circ/2 - \tfrac{1}{2} (\Delta H_D^\circ/K_D)^{1/2}(\phi_L/M)^{1/2} \tag{11}$$

Table I. Calorimetric Data from Titration of 0.009629*M* CuPc in Benzene Solvent into 50.00 ml Benzene at 35.0 ± 0.1°C

Solution no.	Titrant added, ml	Heat of dilution, mcal	ΔH_{obs}, kcal/tot mol
1	0.222	124	2.92
2	0.444	188	2.22
3	0.666	225	1.78
4	0.888	255	1.52
5	1.110	276	1.32
6	1.332	290	1.16
7	1.554	302	1.04
Titrant	...	...	5.00

Table II. Calculation of ΔH_D° for 2 CuPc $\rightleftharpoons$ $(\text{CuPc})_2$ in Benzene at 35.0 ± 0.1°C with $K_D = 8.0 \times 10^3$

Solutions compared	$-\Delta H_D^\circ$, kcal/mol
1, 2	12.3
2, 3	12.4
3, 4	11.2
4, 5	11.8
5, 6	12.1
6, 7	11.2
1, 4	11.4
4, 7	12.5
1, 7	11.7
Average	11.8 ± 0.7 kcal/mol

Table III. Calorimetric Data Taken from Titration of 0.00962_9*M* CuPc in Benzene Solvent into 50.00 ml Benzene at 35.0 ± 0.1°C

Solution no.	Titrant added, ml	Final total CuPc concn	ΔH_{obs}, kcal/tot mol	$-\phi_L$, cal/tot mol	$(-\phi_L/M)^{1/2}$
1	0.222	0.0000425	2.92	2080	6996
2	0.444	0.0000847	2.22	2800	5750
3	0.666	0.0001265	1.78	3220	5045
4	0.888	0.0001679	1.52	3480	4553
5	1.110	0.0002020	1.32	3680	4196
6	1.332	0.0002497	1.16	3840	3922
7	1.554	0.0002901	1.04	3960	3695
Titrant	...	0.009629	5.00	5000	721

Equation 11 relates the heat of dilution, ϕ_L, to the enthalpy of dimerization and to the equilibrium constant for the dimerization process.

Heat of dilution data for CuPc in benzene at 35.0°C are summarized in Table III. From the slope and intercept of a plot, ϕ_L vs. $(\phi_L/M)^{1/2}$, ΔH_D° and K_D may be calculated. From such a plot, the following results are obtained:

$$\Delta H_D^\circ = -12.0 \pm 0.8 \text{ kcal/mol} \tag{12}$$

$$K_D = 9.0 \pm 0.5 \times 10^3 \tag{13}$$

$$\Delta G_D^\circ = -5.6 \pm 1.0 \text{ kcal/mol} \tag{14}$$

$$\Delta S_D^\circ = -21 \pm 4 \text{ cal/deg mol} \tag{15}$$

Discussion

The calorimetric data seem to indicate that the solvated monomer is stabilized as the temperature is increased. At 25°C the enthalpy of dimerization is −10.0 kcal/mol (*4*), but at 35.0°C the enthalpy of dimerization is −12.0 kcal/mol. From the two enthalpies, a value for ΔC_P° may be calculated from Equation 16:

$$\frac{(\Delta H_{T_2}^\circ - \Delta H_{T_1}^\circ)}{(T_2 - T_1)} = \Delta C_P^\circ \tag{16}$$

From the data and the equation, ΔC_P° is calculated to be −200 ± 100 cal/deg mol. The heat capacity is dependent upon several things, among which are the heat capacity of the monomer and the dimer. Another important factor is the degree of solvation of monomer and dimer. To a first approximation, the heat capacity of the monomer is one half of the heat capacity of the dimer. Thus, the change in the heat capacity may be an indication of the relative numbers of solvation benzene molecules for monomers and dimer. Since $\Delta C_P^\circ = \bar{C}_P^\circ$ (dimer) $- 2\,\bar{C}_P^\circ$ (monomer) $= -200 \pm 100$ cal/deg mol, we conclude that the two monomer molecules are surrounded by more benzene solvent molecules than the dimer molecule. Taking $\bar{C}_P$ (benzene) × 32 cal/deg, we conclude that the dimerization process probably involves the release of 6 ± 3 benzene solvent molecules, or 3 solvent molecules per monomer.

These calorimetric studies have helped elucidate some of the intricacies of the dimerization of the metal(II) phthalocyanines. They have also shown that the calorimetric approach is a useful supplement to the more traditional approach of spectrophotometry.

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