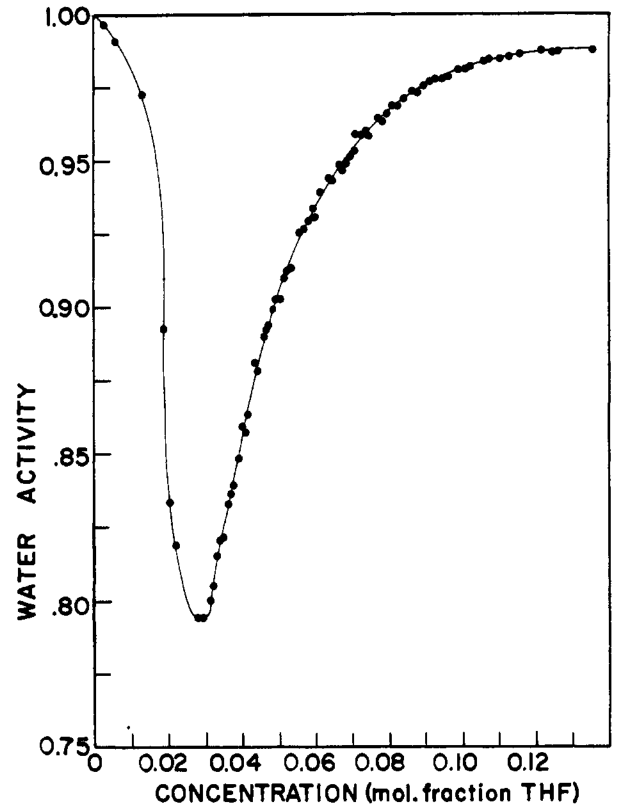

Figure 2. Expanded graph of activity of water at low THF concentrations

occurred in the melting point of the hydrate (*4, 10*), the viscosity (*9*), and the freezing rate (*8*) of the solutions. However, the accuracy of the data is not sufficient to make any definitive statement about this phenomena.

Nomenclature

a_1 = activity of THF
a_2 = activity of water
t = temperature, °C
x_1 = liquid concentration, mole fraction THF
y_1 = vapor concentration, mole fraction THF
α_{12} = relative volatility THF/H_2O
α_{21} = relative volatility H_2O/THF
γ_1 = activity coefficient THF (mole fraction THF)$^{-1}$
γ_2 = activity coefficient water (mole fraction water)$^{-1}$

Literature Cited

(1) Arm, H., *Helv. Chim. Acta,* **53** (3), 465 (1970).
(2) Cigna, R., Sebastiani, E., *Ann. Chim.*, **54**, 1047 (1964).
(3) Crotogino, R. H., BASc thesis, University of British Columbia, Vancouver, B.C., Canada, 1966.
(4) Erva, J., *Suom. Kemistilehti,* **29B,** 183 (1956).
(5) Ferguson, L. N., *J. Amer. Chem. Soc.*, **77,** 5288 (1955).
(6) Glew, D. N., Mak, H. D., Rath, N. S., in "Hydrogen Bonded Solvent Systems," A. K. Covington and P. Jones, Eds., pp 195–210, Proc. Symp. of Equil. and Reaction Kinetics in Hydrogen Bonded Solvent Systems, Taylor & Francis Ltd., London, England, 1968.
(7) Palmer, H. A., PhD thesis, University of Oklahoma, Norman, Okla., 1950.
(8) Pinder, K. L., *Can. J. Chem. Eng.*, **43,** 271 (1965).
(9) Pinder, K. L., *ibid.*, p 274.
(10) Thorpe, B. H., Pinder, K. L., *Suom. Kemistilehti,* **38B,** 243 (1965).

Received for review July 20, 1972. Accepted April 14, 1973. Financial support of this work by the National Research Council of Canada and the University of British Columbia is greatly appreciated.

Molecular Associations in Nonaqueous Solvents
I. Thermodynamics of Dye–Dye Interactions in CCl_4 and C_6H_6

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The thermodynamic parameters of the dimerization of 4, 4′,4′′,4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine in benzene and carbon tetrachloride were determined by an adiabatic calorimetric technique. The values for the dimerization in benzene were $\Delta H_1° = -10 \pm 1$ kcal/mol, $\Delta G_1° = -5.6 \pm 0.1$ kcal/mol, and $\Delta S_1° = -15 \pm 4$ cal/deg. On the basis of the reported values for the dimerization in benzene, the values for the dimerization in carbon tetrachloride were estimated to be $\Delta H_1° \approx -13$ kcal/mol, $\Delta G_1° \approx -8.7$ kcal/mol, and $\Delta S_1° \approx -15$ cal/deg. These results are compared with previously reported values for the dimerization of aqueous metal phthalocyanine ions and other dimerizations in solvents of low dielectric strength.

Metal phthalocyanine dyes, of which 4, 4′, 4′′, 4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine, CuPc (Figure 1), is an example, provide analogs to the biologically important porphyrin skeleton of chlorophyll and the heme moiety of hemoglobin. Additionally, the solid-state interactions of these dyes can be simulated in solution by matching solvent properties and structure solubility characteristics (*6*). Several spectroscopic studies of water-soluble metal complexes of tetrasulfonated phthalocyanine ions (*1, 4*) and descriptions of the dimerization process (*7, 9*) of these charged species have appeared in the literature. However, until recently, little work had been done on phthalocyanine metal(II) dyes in solvents of low dielectric strength (*6*), where the impetus toward dimerization is the dye–dye interaction. Therefore, it is our purpose to investigate systematically the parameters of dimerization in solvents of low dielectric constant, specifically benzene and carbon tetrachloride.

Experimental

Calorimetric titration measurements of enthalpies of dilution of CuPc in benzene and carbon tetrachloride 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

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the reaction vessel after equilibration to the bath temperature (2). All results of our calorimetric measurements refer to 25.0° ± 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. All solvents used in the calorimetric measurements were previously doubly distilled and stored over Lindemann molecular sieves. The water content of each solvent was determined by Karl Fischer titration to be less than 0.07 mg H_2O/ml solvent. The CuPc used was thrice recrystallized from a chloroform-methanol mixed solvent system (*6*).

Results

Calorimetric measurements for addition of 0.01006*M* CuPc in benzene solvent to pure benzene are summarized in Table I. The rather small net heat involved with the dilution process is the result of the very large value of the dimerization constant, $K_1 = 1.6 \times 10^4$ for Reaction 1 in benzene solvent (*6*).

$$2\text{CuPc} \overset{K_1}{\rightleftharpoons} (\text{CuPc})_2 \qquad (1)$$

We have calculated a value of $\Delta H_1°$ for Reaction 1 in benzene solvent from the data in Table I by the following procedure.

(i) Calculate the number of moles of dimer $(\text{CuPc})_2$ in each solution in Table I by use of Equations 2 and 3.

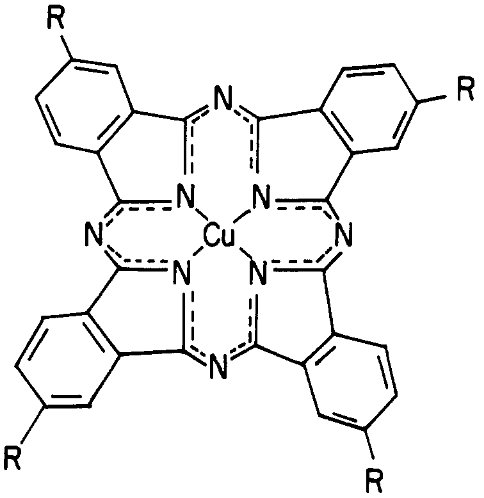

Figure 1. Monomer of 4, 4′, 4″, 4‴-tetraoctadecylsulfonamido copper(II) phthalocyanine molecule where *R* is $SO_2NH(CH_2)_{17}CH_3$

Table I. Typical Calorimetric Enthalpies of Dilution for Titration of 0.01006$_4$*M* CuPc in Benzene Solvent into 50.00 ml Benzene at 25.0 ± 0.1°C

Solution no.	Titrant added, ml	Heat of dilution, mcal		ΔH_{obs} = Heat of dilution / Total moles CuPc	
		Run 1	Run 2	Run 1	Run 2
1	0.222	5.4	5.2	2.4_2	2.3_4
2	0.444	8.5	8.3	1.9_0	1.8_6
3	0.666	10.2	9.9	1.5_3	1.4_8
4	0.888	11.2	11.4	1.25	1.28
5	1.110	12.3	12.6	1.10	1.13
6	1.332	13.1	13.8	0.98	1.03
7	1.554	13.9	14.7	0.89	0.94
8	1.776	14.7	15.5	0.82	0.87

$$K_D = [(\text{CuPc})_2]/[\text{CuPc}]^2 = 1.6 \times 10^4 \qquad (2)$$

$$[\text{CuPc}] + 2[(\text{CuPc})_2] = (\text{ml titrant})(0.01006)/(50.00 + \text{ml titrant}) \qquad (3)$$

(ii) Compare pairs of resulting solutions (*k* and *l*) in Table II with Equations 4 and 5.

$$[(\Delta H_{obs})_k - (\Delta H_{obs})_l]/(\delta_k - \delta_l) = \Delta H_1° \qquad (4)$$

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

In Equation 4, $\Delta H_1°$ represents the molar enthalpy for Reaction 1.

(iii) Use the average value of ΔH_1 values calculated in (ii) to calculate a "better" value of K_1 valid at 25°C by using the van't Hoff equation.

(iv) Repeat (i)-(iii) as necessary. The procedure in step (ii) is used because it eliminates the necessity of inclusion in the calculations of the possibility that higher polymers, $(\text{CuPc})_n$ with $n \geq 3$, may be contained in the relatively concentrated titrant solutions, since this inclusion would interfere with the monomer-dimer model used here (*6, 10, 11*). We have assumed that all measured heats of dilution are the results of reaction only, and that any "nonideal" solute-solute or solute-solvent heats of interaction are negligible when compared to the reaction heats (*10, 11*). We also assume that all activity coefficients are unity in these solutions (*10, 11*).

Results of following steps (i)-(iii) with $K_1 = 1.6 \times 10^4$ are given in Table II for several pairs of solutions listed in Table I. From further application of steps (i)-(iv) we estimate that the "best" values of the thermodynamic quantities for the dimerization Reaction 1 of CuPc in benzene at 25°C are:

$$K_1 = 1.3 \times 10^4 \ (\pm 0.2 \times 10^4)$$
$$\Delta G_1° = -5.6 \ (\pm 0.1) \text{ kcal/mol}$$
$$\Delta H_1° = -10.0 \ (\pm 1.0) \text{ kcal/mol}$$
$$\Delta S_1° = -15.0 \ (\pm 4.0) \text{ cal/deg}$$

The uncertainties shown are reasonable estimates of experimental error.

Because of the even greater stability of $(\text{CuPc})_2$ in carbon tetrachloride ($K_1 = 3 \times 10^6$ at 22°C) (*6*), measured enthalpies of dilution of 0.01*M* solutions of CuPc in CCl_4 are so small that they are highly uncertain. However, from the results obtained in benzene, one can approximate a $\Delta S_1° \approx -15$ cal/deg for Reaction 1 in CCl_4 solvent at 25°C. If this estimate is correct, we can give the following values of thermodynamic quantities for Reaction 1 in CCl_4 at 25°C:

$$K_1 = 2.4 \times 10^6 \ (\pm 0.5 \times 10^6)$$
$$\Delta G_1° = -8.7 \ (\pm 0.1) \text{ kcal/mol}$$
$$\Delta H_1° \sim -13 \text{ kcal/mol}$$
$$\Delta S_1° \sim -15 \text{ cal/deg}$$

Discussion

The dimerization model as proposed in Reaction 1 is substantiated by several important facts. The first of these are the spectroscopic results of Monahan et al. (*6*) which support only the dimerization model. References cited in Ref. *11* also indicate that at low concentrations (such as those with which we are here concerned), the only important aggregate is the dimer for such molecules as carboxylic acids in nonaqueous solvents.

Table II. Representative Calculations of $\Delta H_1°$ for Dimerization of CuPc in Benzene at 25°C from Data in Table I by Use of $K_1 = 1.6 \times 10^4$

Solutions compared, k, l	$-\Delta H_1°$, kcal, Run 1	$-\Delta H_1°$, kcal, Run 2
1, 2	9.0	8.3
2, 3	12.1	12.4
3, 4	14.0	10.0
4, 5	10.4	10.4
5, 6	10.8	9.0
6, 7	10.2	10.2
7, 8	9.6	9.6
1, 4	10.8	9.8
4, 8	10.3	9.8
1, 8	10.7	9.8

The results of our calorimetric measurements also indicate that only dimers are present for the following reasons. As noted in Table II, $\Delta H_1°$ is not a function of the concentration of the CuPc in the reaction vessel. If higher polymers were present, a systematic increase or decrease in $\Delta H_1°$ would appear as the concentration of CuPc in the reaction vessel increases. However, as previously stated, $\Delta H_1°$ is not a function of the formal concentration of CuPc except for random scatter. Furthermore, dimers are considered to be primary aggregates since including trimers or higher aggregates does not improve the fit of the data.

Comparison of these thermodynamic results with similar studies yields some interesting observations. Hammes and Park (*3*) and Kyogoku et al. (*5*) reported an entropy of dimerization of 1-cyclohexyluracil in chloroform as -14.5 and -11.0 cal/deg, respectively. Kyogoku et al. (*5*) also studied the dimerization of ethyladenine in chloroform and reported an entropy of dimerization equal to -11.4 cal/deg. Additionally, Woolley et al. (*10*) reported a $\Delta S_{298}°$ value of -25.6 cal/deg for the trimerization of phenol in benzene and carbon tetrachloride. Thus, the $\Delta S_1° = -15$ cal/deg reported here is in good agreement with other dimerizations in solvents of low dielectric constant and appears to show the proper statistical entropic contribution when compared to trimerization in solvents of low dielectric strength.

More interestingly, our calorimetric thermodynamic data rather closely resemble those for the dimerization of aqueous cobalt(II)-4, 4′, 4″, 4‴-tetrasulfophthalocyanine ion obtained from the temperature dependence of the spectrophotometrically determined equilibrium constant, reported by Schelly et al. (*8*). They found a $\Delta H_1°$ for dimerization equal to -14 kcal/mol, $\Delta S_{331}° = -18$ cal/deg, and $\Delta G_{331}° = -8$ kcal/mol. These results seem to indicate an insignificant role of solvent participation in phthalocyanine dimerization.

Calorimetric studies of this type, in addition to stopped flow kinetic studies of the dimerization, should eventually permit an interpretation of both the π–π interaction and central atom participation in dimerization and higher aggregation in porphyrin-type systems.

Acknowledgment

The authors thank Alan R. Monahan of Xerox Corp. for a generous supply of CuPc.

Literature Cited

(1) Bernauer, K., Fallab, S., *Helv. Chim. Acta*, **44**, 1287 (1961).
(2) Graham, R. C., PhD dissertation, University of Utah, Salt Lake City, Utah, 1972.
(3) Hammes, G. G., Park, A. C., *J. Amer. Chem. Soc.*, **90**, 4151 (1968).
(4) Kobayashi, H., Torri, Y., Fukuda, N., *J. Chem. Soc. Jap.*, **81**, 694 (1960).
(5) Kyogoku, Y., Lord, R. C., Rich, A., *J. Amer. Chem. Soc.*, **89**, 496 (1972).
(6) Monahan, A. R., Brado, J. A., DeLuca, A. F., *J. Phys. Chem.*, **76**, 446 (1972).
(7) Schelly, Z., Farina, R. D., Eyring, E. M., *ibid.*, **74**, 617 (1970).
(8) Schelly, Z. A., Harward, D. J., Hemmes, P., Eyring, E. M., *ibid.*, **75**, 3040 (1970).
(9) Shepperd, S. E., Geddes, A. C., *J. Amer. Chem. Soc.*, **66**, 1995 (1944).
(10) Woolley, E. M., Travers, J. G., Erno, B. P., Hepler, L. G., *J. Phys. Chem.*, **75**, 3591 (1971).
(11) Zaŭgg, N. S., Steed, S. P., Woolley, E. M., *Thermochim. Acta*, **3**, 349 (1972).

Received for review July 28, 1972. Accepted April 19, 1973. The authors thank the Directorate of Chemical Sciences, Air Force Office of Scientific Research, for Grant No. AFOSR 69-1717 and Brigham Young University Research Division for financial support.