The J-aggregate of Meso substituted Thiacarbocyanines in MeOH Solution

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Abstract

To take an information of substitutent effect and thermodynamic of J-aggregate at thiacarbocyanines, association constant K_J, free energy of association G_J, enthalpies of J-aggregate H_J were measured by spectrophotometer according to dependence on con centration of dyes and temperature of aqueous MeOH and KCl salted-out system.

With increase of concentration of dyes or decrease of temperature of aqueous MeOH system, absorption spectra of dyes exhibited equlilibria shift toward the aggregate. Ph enyl meso substituted thiacarbocyanine, DyeIII, resulted in higher K_J and G_J values th an DyeI and DyeII. To easily make J-aggregate of thiacarbocyanine, meso substitutie nt group need to be a flat structure, which will make a park as well as lain tiles.

요 약

Meso 치환 thiacarbocyanine 색소의 J-aggregate 형성시 치환기 효과와 열역학적인 정보를 얻기 위한 수단으로 UV/Vis 분광기를 이용하여 색소농도변화에 따른 회합정수K_J,

회합자유에너지 G_J, 회합엔탈피 H_J를 구하였다. 그 결과 농도증가와 함께 J-aggregate의 생성이 증가하였으며 온도감소와 함께 J-aggregate형성쪽으로 회합평형상수가 이동하였다. 치환기 효과로는 phenyl기의 치환이 평면구조를 형성하는데 있어서는 methyl, ethyl기 치환체보다 회합체형성이 유리하였으며 회합자유에너지와 회합엔탈피도 alkyl기 치환체보다 증가하였다.

I. Introduction

The appearance of J-band is extraordinary spectral phenomenon by molecular association. This phenomena were first noted by Jelley[1] and Scheibe[2], its origin has been discussed by many researcher. Herz[3] has reviewed the aggregation of organic dyes in solution but only a few dyes are known to form the J-aggregate in solution. The aggregation number of the J-aggregate is not firmly fixed; different numbers, n = 3-7, have been proposed for pseudoisocyanine (1,1″-diethyl-2,2″-cyanine chloride).

Makio and co-worker[4] studied thermodynanics of J-aggregate of 5,5″6,6″-Tetrachloro-1,1″-diethyl-3,3″-bis(4-sulfobutyl)-benzimidazolo-carbocyanine sodium salt in dilute NaOH aqueous solution(pH=11.0), and at the results, the association number is estimated to be 8, the entropy change for the association are found as ΔH = -91.5 kcal/mol and ΔS = -139.3 kcal/mol, respectively.

Up to today, even though thermodynamics of J-aggregate for cyanine dyes have been studied by many researchers , J-aggregate of meso substituted cyanines are made few study. In this present paper, we reports thermodynamics of the J-aggregate of meso substiuted thiacarbocyanines, such as association numbers, free energy, and enthalphies of association in aqueous MeOH solution with KCl .

II. Experimental

Thiacarbocyanine dyes used in this study were substituted in meso position with methyl, ethyl and phenyl group. (Fig.1) These dyes were supplied from Nihonkankoshikiso Co.,and were used without further purification.
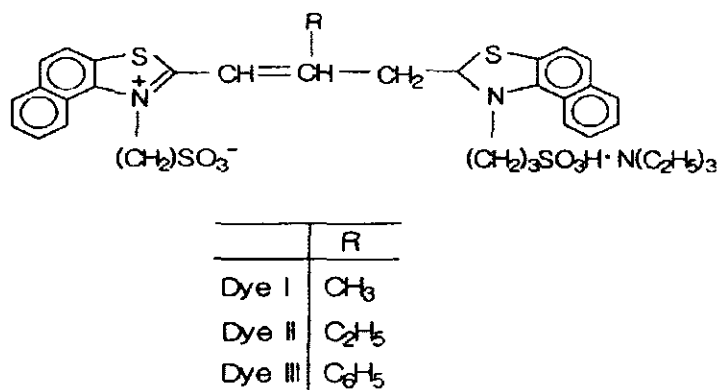
Fig. 1. Structure of thiacarbocyanines.

In general, a stock solution was prepared by dissolving them in MeOH, because these dyes tend to undergo irreversible and nonreproducible aggregation in water. Immediately before use, the solution was diluted with diluted water and MeOH to make typically 10 vol % aqueous MeOH solutions for the study of J-aggregation equilibrium.

For typical experimental conditions, J-aggregation equilibrium was reached almost instantaneously by the salted-out KCl solution in place of water. UV/Vis absorption spectra were measured with a conventional spectrophotometer, UV/Vis-2101 Shimadzu Co., LTD..

III. Results and Discussion

A typical spectra changed by the dye aggregation is shown in Fig.2 for the concentration range $10^{-6} mol/dm^3$ at 25℃. J-aggregation of cyanine dyes from concentrated aqueous solution is analogous to the precipitation of sparingly soluble salts.[5] Aggregates of large size or even crystallites, which can be regarded as a solid phase and the monomer in solution, whose concentration corresponds to the solubility of the solid aggregate.

1.5

10^{-2} M KCl
10% Me OH
Cell · 1cm
25 ℃

Absorbance

1.0

1. 7.62 × 10^{-6} M
2. 5.72
3. 4.29
4 3.30

1
2
3
4

Dye III

0.5

0.0

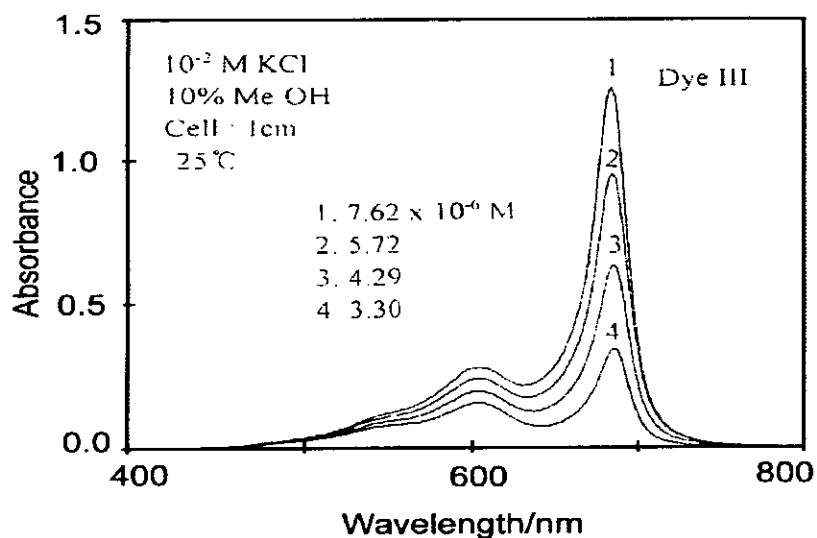400   600   800

Wavelength/nm

Fig. 2. Monomer-J-aggregate absorption spectra changes of DyeIII according to various concentration in 10% MeOH solution containing KCl.

In moderately dilute solutions containing electrolytes, however, some dyes form small, stable J-aggregate particles, each consisting of a few monomers and having little chance to grow. The equilibrium between particle and monomer is described as

$$nM \longleftrightarrow J \qquad (1)$$
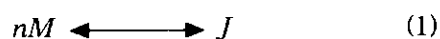
and the equilibrium constant, K_J, is given by

$$K_J = c_J \ / \ (c_M)^n \qquad (2)$$

where c_J and n are the concentration and association number of the aggregate particles, repectively.[4]

J-aggregation in diluted Dye III solutions containing MeOH and KCl is a phenomenon of this kind. Fig.2 show the absorption spectra of Dye III solution of four different concentrations in 10% MeOH containing 10^{-2} mol/dm^3 KCl at 25℃. Reversible variation with temperature of one of these specta is shown in Fig.3, where

the isosbestic point at about 601 nm verifies the equilibrium holding.

These figures correspond to nature for dimerization, and were analyzed in a similar way.[6] Because the overlap of J-band at the wavelength of the monomer peak was considered to be minimum at the lowest total dye concentration, the equilibrium monomer concentration was determined under such a condition as the ratio of the measured monomer band absorbance A to the molar absorption coefficient determined from Eq. (3)

$$A = (\varepsilon^2_M \, l^2/K_J) \, (\, c/A) - {}_Ml/K_J \qquad (3)$$

Where l is the solution thickness.

If the sole solute species are monomers and J-aggregates, then plotting A against c/A should give a straight line of slope ${}^2_M \, l^2/K_J$ and intercept - ${}_Ml/K_J$, from which both K_J and ε_M can be determined. The concentration of J-aggregated monomers was calculated as $c-c_M$.
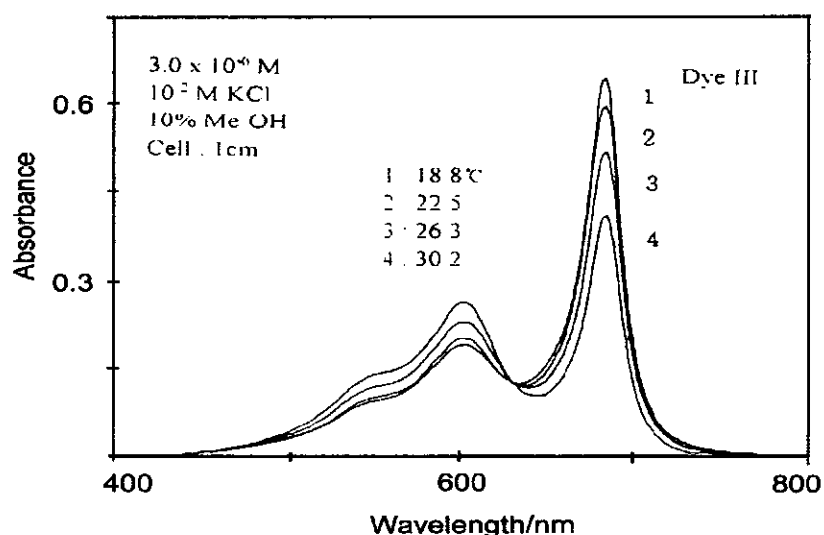

Fig. 3. Absorption spectra changes of Dye III according to various temperatures in 10% MeOH solution with KCl.

From this and the measured J-band absorbance we estimated the molar absorption

coefficient of J-aggregted monomers at 6.85 $10^6 dm^3$/mol. The $_J$ was then used for calculating nc_J and c_M of solutions of higher dye concentrations from their J-band absorbance.

The value of n was determined as the slope of a conventional $\log c_J$ versus $\log c_M$ plot. Such plots are shown in Fig. 4 for five different temperature from about 4 to about 7, reflecting the large dissocition degree of small particles at higher temperatures. This is contrast with the result of Makio et al. and Matsubara et al., who obtained a temperature independent association number of 8 for an anionic benzimidazolocarbocyanine.[4]Even in our case, n in all dyes was approximately constant at 5 between 20 and 25 ℃. Thermodynamic quantities or the J-aggregations of Dyes used in this study were therefore determined at 5 between 20 and 25 ℃ for n = 5. If applied eq.(2) at DyeIII, K_J was calculated to be 9.3 $\times 10^{17}$ dm^9/mol^3 at 20℃ and be 4.1 $\times 10^{17}$ dm^9/mol^3 at 25℃, both giving approximately the same ΔG_J of -25 kcal/mol-pentamer according to (eq.4)

$$G_J = - RT \ln K_J \qquad (4)$$

The enthalpy of J-aggregation ΔH_J was determined from the slope of log K_J versus $1/T$ plot (Fig.5), using the equation

$$d \ln K_J \, / \, d(1/T) = -\Delta H_J \, / \, R \qquad (5)$$

and was -41.9 kcal/mol-pentamer. These K_J , ΔG_J and ΔH_J values of all Dyes are also listed in table1.

Our ΔH_J value corresponds to a mean aggregation enthalpy of about -11 kcal/mol-monomer in aggregate and may be compared with that of Makio et al. For an anionic benzimidazolocarbocyanine (-91.5 kcal/mol-octamer, or -11.4kcal/mol-monomer).

Also, we have obtained an enthalpy of 11 kcal/mol for the monomer diassociation from salted-out J-aggregate of 1,1'-diethyl-2,2'cyanine.[7] These valuse suggest that a mean stabilization by about 11 kcal/mol-monomer is a condition for the reversible J-aggregation. Less than one-third of this stabilization is enough for dimerization (3.4 kcal/mol-monomer for DyeIII in 10% MeOH.[6] Such comparison in meso-substituted thiacarbocyanines has become possible only with our first set of thermodynamics.
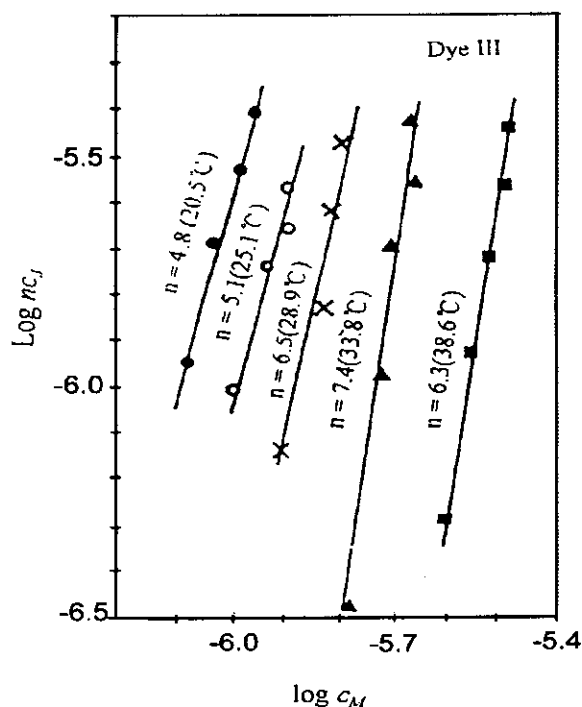
Fig. 4. Log cn_J versus log c_M plots, showing n
to be temperature - dependence.

Table 1. Thermodynamic Quantities for the aggregate of Dyes.

| Aggregate Solvent		J-pentamer
Dye I	Association constant K_J	$8.9 \times 10^{11} dm^3/mol$ (20°C)
	Free energy of association G_J	-24.2Kcal/mol-pentamer (20-30°C)
	Enthalphy of association H_J	-38.6Kcal/mol-pentamer (20-30°C)
Dye II	Association constant K_J	$9.1 \times 10^{11} dm^3/mol$ (20°C)
	Free energy of association G_J	24.8Kcal/mol- pentamer (20-30°C)
	Enthalphy of association H_J	6.2Kcal/mol- pentamer (10-30°C)
Dye III	Association constant K_J	$9.3 \times 10^{11} dm^3/mol$ (20°C)
	Free energy of association G_J	-25.0Kcal/mol- pentamer (20-30°C)
	Enthalphy of association H_J	-41.9Kcal/mol- pentamer (20-30°C)
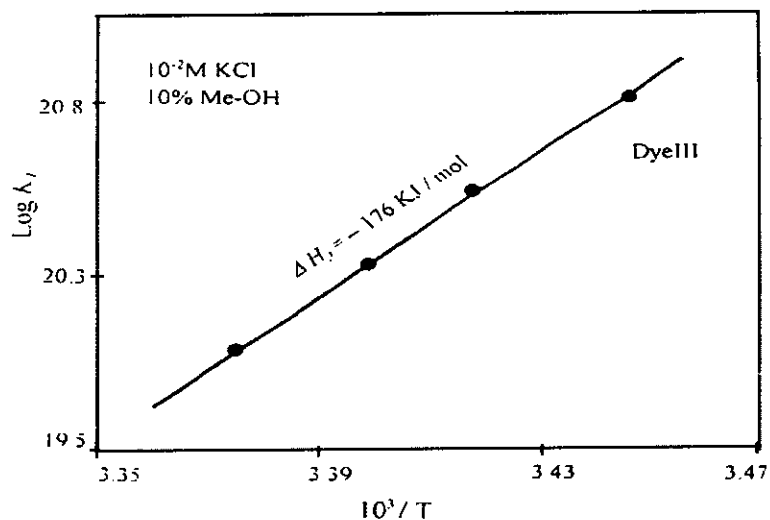
Fig. 5. Log K_J versus $1/T$ plot for determining ΔH_J.

IV. Conclusion

Spectrophotometric study of the J-aggregation equilibrium of meso-substituted thiacarbocyanines in aqueous MeOH soluions with KCl has allowed the determination of J-aggregate constant, free energy, and enthalpy. The association number depends on temperature, being larger at higher temperatures. The enthalpy loss due to J-aggregation is about 11 kcal/mol-dye monomer, whereas only less than one-third of this loss is due to dimerization.[6]

Reference

(1) E.E Jelley, Nature, 138, 1009 (1936)

(2) G.Scheibe, angew. Chem.,49, 563 (1936)

(3) H.Herz, photogr. Sci. Eng., 18,323 (1974)

(4) S.Makio et al., Bull. Chem. Soc.Jpn., 53,3120 (1980)

(5) E.Daltrozzo,et al, Photogr. Sci. Technol., 18, 441 (1974)

(6) S.M.Son, J.Kor.Prin.Soc.,18,125 (2000)

(7) T.Tanaka,et al, Nippon Shashin gakkaishi, 50, 22 (1987)