

Thermodynamics of Meso substituted Thiocarboyanines in Solution

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(2000년 7월 22일 접수, 2000년 8월 19일 최종 수정본 접수)

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(Received 22 July 2000, in final form 19 August 2000)

Abstract

To take an information of substituent effect and thermodynamic of association at thiocarboyanines, association constant K_D , free energy of association ΔG_D , enthalpies of association ΔH_D were measured by spectrophotometer according to dependence on concentration of dyes and temperature of aqueous MeOH system.

With increase of concentration dyes or decrease of temperature of aqueous MeOH system, absorption spectra of dyes exhibited equilibria shift toward the dimer. Phenyl meso substituted thiocarboyanine, DyeIII, resulted in higher K_D and ΔG_D values than DyeI and DyeII. To easily make an association of thiocarboyanine, meso substituent group need to be a flat structure, which will make a park as well as lain tiles.

요약

Meso 치환 thiocarboyanine 색소의 회합체 형성시 치환기 효과와 열역학적인 정보를 얻기 위한 수단으로 UV/Vis 분광기를 이용하여 색소농도 변화에 따른 회합정수 K_D , 회합자유에너지 ΔG_D , 회합엔탈피 ΔH_D 를 구하였다.

그 결과 농도 증가와 함께 Dimer 의 생성이 증가하였으며 온도감소와 함께 Dimer 형성쪽으로 회합평형상수가 이동하였다. 치환기 효과로는 phenyl 기의 치환이 평면 구조를 형성하는데 있어서 methyl, ethyl 기 치환체보다 회합체형성이 유리하였으며 회합자유에너지와 회합엔탈피도 alkyl 기 치환체보다 증가하였다.

1. Introduction

Interactions among dye molecules generate large spectral shifts and distinct changes in band shape. For a singles dye or a mixture of dyes, increased concentrations can lead to either progressive shifts of absorption maxima to shorter wavelength (H-aggregates) or abrupt shifts to longer wavelength(J-aggregates). These phenomena were first noted by Jelley¹⁾ and Scheibe²⁾ and have been studied by many researchers up to today.

In general, molecules of many cyanine dyes associate in aqueous media to form either H-aggregates (dimers, trimers, etc) or j-aggregates. Spectral changes have been used to determine the association number for aggregates, as well as the thermodynamic quantities for aggregates, such as association constants, free energy and enthalpies of association.

West et al³⁾ studied systematically the monomer-dimer equilibria of the vinylogous series of meso unsubstituted cationic 3,3'-diethylthiacyanine dyes in aqueous solution after graphically separating the overlapping monomer and dimer absorption bands into each component by successive approximations. And also they reported that the dimer dissociation constant $1/K_D$ (K_D : association constant) decreased and the free energy of dissociation $-\Delta G_D$ increased with increased methine chain length.

Padday³⁾ determined the equilibrium constants, free energy, entropies, and enthalpies of dimerization, as well as of trimerization of 3,3'-dimethyl-9-ethylthiacarbocynine bromide in aqueous solution at 20-60°C, assuming all the dye molecules that were neither monomers nor dimers to be H-trimers. He reported that the dimerization enthalphy H_D of 3,3'-dimethyl-9-ethylthiacarbocynine bromide in aqueous solution was about -5.8kcal/mol.

Herz⁴⁾ extended the analysis to 3,3',9-triethyl-5,5'-dichlorothiacarbo-cyanine chloride and its anionic 3,3'-bis(carboxylethy) analog in dilute aqueous alkaline solution. The net dye charger had no substantial effect on monomer-dimer equilibria, whereas chlorine substitution at the 5-position resulted in somewhat larger free energy of dimerization.

He also reported that J-aggregate of 1,1'-diethyl-3,3'-bis(sulfobutyl)-5,5',6,6'-tetrachlorobenzimidazolocarbo-cyanine was reversible in dilute aqueous alkaline solutions and this dye gave no indication of dimer formation and that the J-aggregate was a tetramer whose free energy of formation amounted to 3-4 times those of dimersization of typical thiacyanines studied. But again no enthalpies of formation were given. The latter dye was studied also by Makio et al.⁶⁾, but with the a formation free energy lager twice than Herz and a formation enthalphy ΔH_J -91.5kcal/mol.

Hayashi et al.⁷⁾ published that the dimeric association constant ΔK_D of four differently substituted thiacyanines in aqueous solution at room temperature in relation to their study of the spectral

sensitization of thermally processed silver salt photographic materials. Though explicit ΔG_D values were not given, their ΔK_D values confirmed dimer stabilization by 5-chlorine as well as 3-sulfopropyl substitution.

More recently, Matsubara et al.⁸⁾ reported determinations of the association numbers, association constants, free energies, and enthalpies of association for 3,3'-bis(sulfopropyl)-5,5'-diphenyl-9-ethyloxacarbo cyanine in aqueous Me-OH solution. According to their report, free energy of association ΔG_D was -24kcal/mol and enthalpy of association ΔH -39kcal/mol for 3,3'-bis(sulfopropyl)-5,5'-diphenyl-9-ethyloxacarbo cyanine.

Up to today, even though thermodynamics of molecular associations for cyanine dyes have been studied by many researcher, meso substituted cyanines are made few study. The present paper reports thermodynamics of meso substituted thiocarboyanines, such as association numbers, free energy, and enthalpies of association in aqueous MeOH solution .

2. Experimental

Thiocarboyanine dyes were supplied from Nihokankoshikiso Co, and were used without further purification. (Fig.1) In these study, these dyes were substituted in meso position with methyl, ethyl and phenyl group.

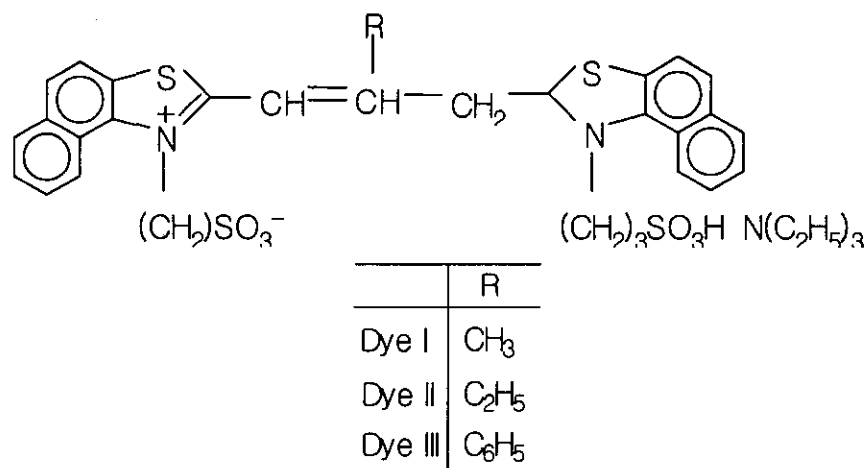


Fig. 1 Structure of thiocarboyanines.

In general, cyanine dyes tend to undergo irreversible, nonproductive aggregates in diluted water, a stock solution was prepared by dissolving them in MeOH. Immediately before use, the solution was diluted with diluted water and MeOH to make typically 10v% aqueous MeOH solutions for the study of dimerization equilibrium.

For typical experimental conditions, associational equilibrium was reached almost instantaneously. UV/Vis absorption spectra were measured with a conventional spectrophotometer, UV-2101 Shimadzu Co., LTD..

3. Results and Discussion

Fig.2 shows spectra of monomeric states of methyl, ethyl, and phenyl substituted thiacyanine in MeOH solution, main absorption peaks of them were 572nm, 578nm, and 601nm respectively. The main peak, monomeric absorption state of Dye III, meso substituted thiacyanine (DyeIII) with phenyl ring, is longer wavelength than alkyl groups, since $\pi-\pi^*$ transition in DyeIII is rich. Fig.3 shows equilibriums of the monomeric and dimeric state according to different concentrations in 10% MeOH solution.

The shoulders at about 560nm, 544nm, and 537nm respectively are a vibrational structures of the monomer band overlapped by the dimer band. The vibrational structures exist in the spectra of DyeI, DyeII, and DyeIII in MeOH as well.

The dimer band peaks are characteristic of aqueous solution and its intensity relative to the monomer band increased with increasing dye concentration.

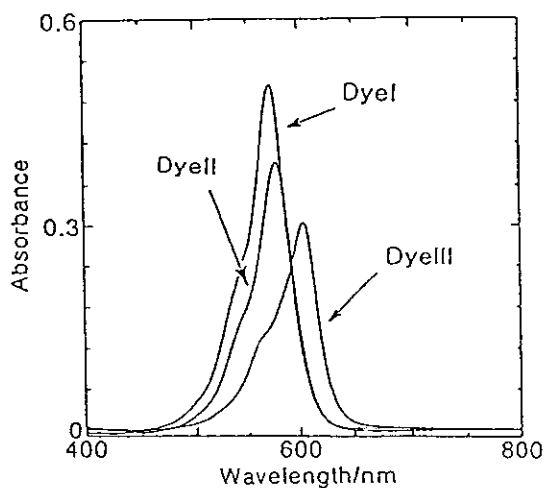


Fig.2 Absorption spectra of thiacyanines in MeOH solution.

Harris and hobbs' equation was given the dimer association constant K_D and the molar absorption coefficient ϵ_M of the monomer simultaneously for the dependence of monomer band absorption A on total dye concentration c ,

$$A = (\epsilon_M^2 l^2 / 2K_D) (c/A) - \epsilon_M l / 2K_D \quad (1)$$

where l is the solution thickness. If the sole solute species are monomers and dimers, then plotting A against c/A should give a straight line of slope $\epsilon_M^2 l^2 / 2K_D$, and intercept $-\epsilon_M l / 2K_D$, from which both K_D and ϵ_M can be determined. Equation (1) can not hold strictly only if net dimer absorbance is not negligible. To approximately fulfill

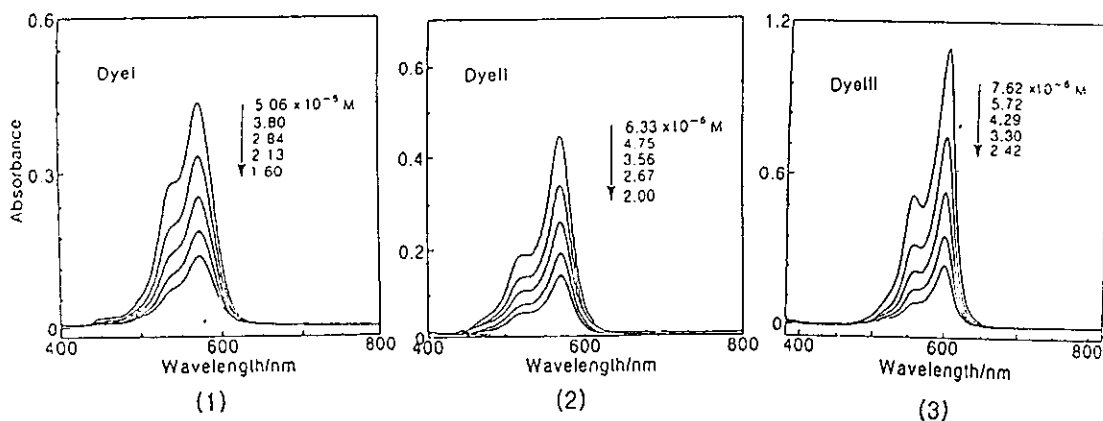
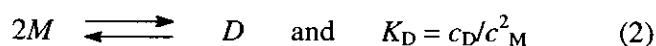


Fig.3 Absorption spectra changes of thiocarboyanines according to various concentration in 10% Me-OH solution.

these conditions, the absorbance at monomer band peak in solution is to controlled in keeping the contribution of dimer absorbance less than about 5%. Fig.4 shows a typical A versus c/A plot giving a fairly straight line, from which, in the case of DyeIII, $K_D = 6.52 \times 10^3 \text{ dm}^3/\text{mol}$ and $\epsilon_M = 6.66 \times 10^4 \text{ dm}^3/\text{mol}$ were obtained at 25°C in 10% MeOH. Concentrations of monomers c_M and of dimers $c_D = (c - c_M)/2$ were calculated using either ϵ_M and A or K_D and c . A conventional plot of $\log c_D$ versus $\log c_M$ gave a straight line of slope 2.0, as shown in Fig.5, confirming the predominance of monomer-dimer equilibrium according to



The free energy of dimerization of DyeIII ΔG_D was given by K_D

$$\Delta G_D = -RT \ln K_D \quad (3)$$

to be $-6.7\text{kcal/mol-dimer}$ at $10-40^\circ\text{C}$. Fig.6 shows the reversible variation with temperature of the absorption spectrum of DyeI solution exhibiting an equilibrium shift toward the dimer with decreasing temperature. from the temperature dependence of K_D the enthalpy of dimerization ΔH_D is given

$$d \ln K_D / d(1/T) = -\Delta H_D / R \quad (4)$$

a plot $\log K_D / c_M$ is given at Fig.7. ΔH_D was constant at $-5.8\text{kcal/mol-dimer}$ between $10-40^\circ\text{C}$. These values of thiocarbocyanine used in this paper are listed at Table 1, with K_D and G_D values. Phenyl meso substituted thiocarbocyanine, DyeIII, resulted in higher K_D and ΔG_D values than DyeI and DyeII. To easily make an association of

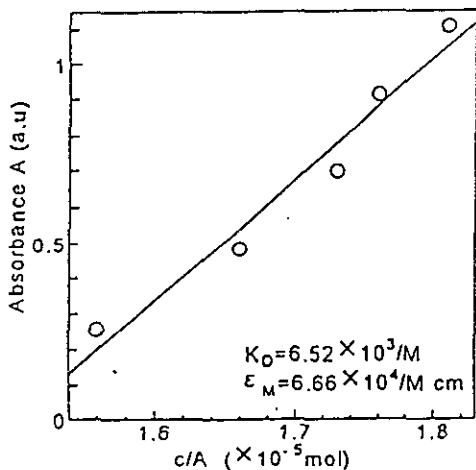


Fig.4 Typical A versus c/A plot for determining K_D and ϵ_M simultaneously at DyeIII in 10% MeOH.

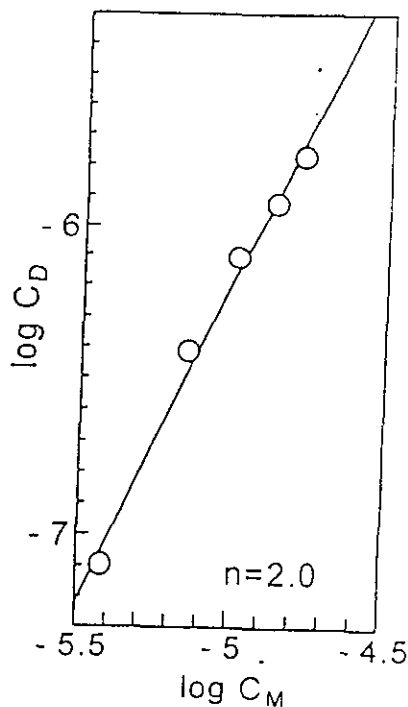


Fig.5 $\log c_D$ versus c_M plot association number 2, confirming the predominance of monomer-dimer equilibrium at DyeIII in 10% MeOH.

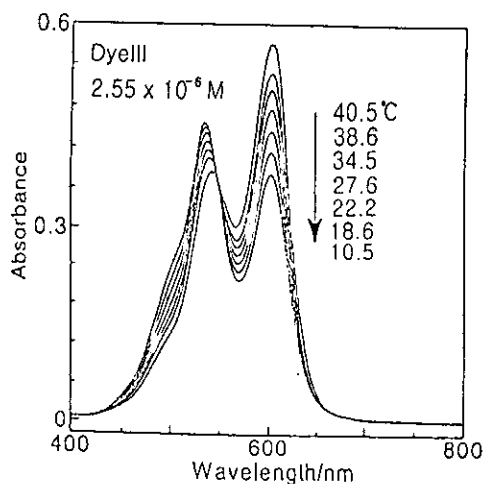


Fig.6 Absorption spectra changes of DyeIII according to various Temperatures in 10% Me-OH solution.

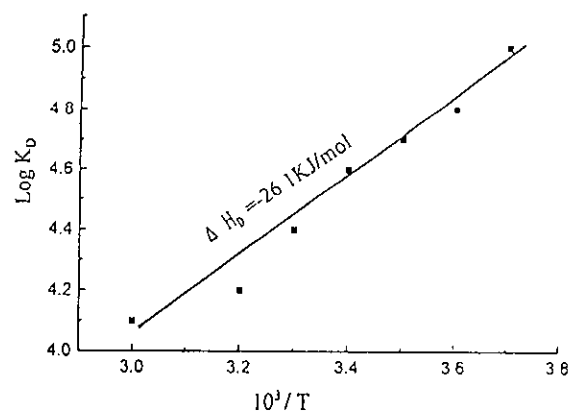


Fig.7 $\log K_D$ versus $1/T$ plot for determining ΔH_D at DyeIII.

thiocarboyanine, meso substituent groups needs to be a flat structure, which will make a park as well as well a plain tile. For the reason of higher K_D and ΔG_D values at DyeIII than at DyeI and DyeII in this paper, author thought that phenyl meso substituent of DyeIII made an easy association than methyl or ethyl mesosubstituted thiocarboyanines. These thermodynamic quantities suggest the importance of meso substituted groups in determining the dimerization behavior of dyes in aqueous alcohol solution.

Table 1 Thermodynamic Quantities for the aggregate of Dyes.

	Association solvent	H-Dimer
DyeI	Association constant K_D Free energy of association ΔG Enthalphy of association ΔH	$5.24 \times 10^3 \text{ dm}^3/\text{mol}(25^\circ\text{C})$ $-6.0 \text{ Kcal/mol-dimer}(10-40^\circ\text{C})$ $-5.7 \text{ kcal/mol-dimer}(10-40^\circ\text{C})$
DyeII	Association constant K_D Free energy of association ΔG Enthalphy of association ΔH	$5.66 \times 10^3 \text{ dm}^3/\text{mol}(25^\circ\text{C})$ $-6.1 \text{ Kcal/mol-dimer}(10-40^\circ\text{C})$ $-5.8 \text{ Kcal/mol-dimer}(10-40^\circ\text{C})$
DyeIII	Association constant K_D Free energy of association ΔG Enthalphy of association ΔH	$6.52 \times 10^3 \text{ dm}^3/\text{mol}(25^\circ\text{C})$ $-6.7 \text{ Kcal/mol-dimer}(10-40^\circ\text{C})$ $-6.2 \text{ Kcal/mol-dimer}(10-40^\circ\text{C})$

4. Conclusion

Spectrophotometric study of the dimerization equilibrium of meso substituted thiocarbocyanines in aqueous MeOH solutions has allowed the dimerization constant, free enthalpy and enthalpy of dimerization. The association number depends on temperature, higher association constant K is higher free energy of association ΔG and Enthalpy of association ΔH .

In the near future, author hope estimatemen of J-aggregation of meso substituted thiocarbocyanine dyes in KC1-aqueous MeOH system by the same method.

Reference

1. E.E.jelley, *Nature*, **138**, 1009(1936)
2. G.Scheibe, *angew. Chem.*, **49**, 563(1936)
3. W.West, S.Pearce, *J.Phys.Chem.*, **69**,1894(1965)
4. J.paddy *J.phys.Chem.*, **75**,1259(1968)
5. A.H.Herz, *photogr.Sci.Eng.*, **18**,323(1974)
6. S.Makio et al., *Bull. Chem. Soc.Jpn.*, **53**,3120(1980)
7. Y.hayashi et al., *J.Imaging Sci.*, **33**,124(1980)
8. T.Matsubara etal., *ibid*, **35**,274(1991)