C:\Aftab1.PM5\11

Material Science Research India Volume 03, No. (1) 43-46 (2005)

J-AGGREGATION OF CARBOCYANINE DYE AND THERMODYNAMIC PROPERTIES

S. Ravi[1] and Jagadish Prabhu[2]

[1]Research and Development, Hindustan Photo Films, ooty (India)
[2]Defence Research and Development Organisation, Bangalore (India)

(Received, October 6, 2003)

ABSTRACT

Apparently reversible and dissociation of small, metastable primary J- aggregate particles and dimeric particles of a phanchromatic carbocyanine dye I in moderatly dilute aqueous methanol solutions containing electrolytes (Kcl and Na_2SO_4) have been studied spectrophotometrically. Association numbers, n, for the particles were estimated from mass action relation between the concentration of free and aggregated dye molecules. Particle sizes, were also estimated from spectral absorption line widths. The thermodynamic properties like equilibrium constant and free energy were calculated. The dye can be efficiently used in photography and in optical memory systems.

INTRODUCTION

The self aggregation of molecules into structurally well defined assemblies which posses distinctive photophysical and optical properties has attracted strong interest over the past years due to the great opportunities for technical application of such materials[1]. By control of the non covalent interactions, different extended supramolecular assemblies could be designed[2-5]. However beyond the field of material science, molecular aggregates also play a fundamental role in living matter, for example, in the processes of photosynthesis[6], biological pigments are non covalently bound to proteins, forming so called pigment protein complexes. Such aggregates serve as light harvesting antennas absorbing light energy, which is eventually transferred over many chlorophyll molecules towards the phosynthetic assemblies of synthetic dyes, such as the well known J- aggregates have become popular model systems[7,8]. J-aggregation of cyanine dyes attracted attention of many scientists and technologists, not only because of their importance in spectral sensitisation of silver halide photographic materials[8] but also because of their potential applicability to multi frequency optical memory systems[10]. The existence of stable J- aggregates in aqueous solution is evidenced by light scattering and demonstrated by solution centrifugation and electron microscopy[9,10]. Since the discovery of the J-aggregate properties including the thermodynamic properties of the blue and green region sensitising dyes in solution have been studied thoroughly and systematically[11-14]. The properties of red region sensitising cyanine dyes in solution, however have seldom been reported. In the work presented here a red sensitising Carbocyanine Dye I 1-ethyl -2- {3-(1-ethyl naptho [1,2-d] thiazolin - 2-ylidine)-propenyl} naptho [1,2,-d] thiazolium iodide was chosen and studied. Dyes with similar structure are used as biological stains which are useful for the characterisation of nucleic acids on gel, and to differentiate phosphoproteins, such as casein from non phosphorylated proteins apart

from photography.

EXPERIMENTAL

The Dye I was supplied by Riedel.de.Haen chemicals and has been used as such. High performance liquid chromatography (HPLC) showed no impurities. The effective molecular mass was taken to be 592 g/mol. Stock solutions of $2.5x10^{-4}$ M dye were prepared through stirring at room temperature for atleast 12 hours. For spectroscopic measurements, the solutions were diluted to $2.5x10^{-5}$, $1x10^{-5}$, $2.5x\ 10^{-6}$M, $5x10^{-6}$M and $7.5x10^{-6}$M. with in the experimental limits of error, the spectra from different stock solutions were reproducible. The absorption spectra were measured with a shimadzu UV-240 spectrophotometer at 25°C between 400nm and 700nm.

RESULTS AND DISCUSSION

The Dye I self associates easily in aqueous solution to form dimers at a very low concentration. The absorption spectra of Dye I (fig. 1) of different concentration in 10% aqueous methanol and comparing the spectra with those of the dye in methanol the peaks at 574nm and 560nm were ascribed to monomer (M) and dimer (D) band respectively the absorption spectrum in methanol was used for determining $\in_m$ value of $7.13x10^3$ dm^3/mol.cm and the absorption line width W_M of free monomer we can use $\in_m$ A and the following equation to calculate the monomeric, C_M , and dimeric concentration, C_D

$$C_D = C\text{-}C_M/2$$

For each total dye concentration C, equilibrium free monomer concentration, C_M was determined from measured monomer band absorbance and 0. A plot of log C_D versus log C_M (fig. 4) shows a straight line of slope approximately 2 indicating that there is an equilibrium between monomers and dimers in the solution which can be described as

$$2M \rightleftharpoons D$$

Therefore $K_D = C_D / C_M^2$ was calculated as $1.112x10^4$ dm^3/mol and the free energy $\Delta G_D = -RT\ln K_D$ as $-2.5Ox10^{-2}$ Kcal/mol.

The electrolytes Kcl and Na_2So_4 in the dye solutions promotes the J-aggregate system organisation (fig. 2 and 3). It exhibits the monomer peak at 574nm and a predominant J-band peak at 650nm and there exists an equilibrium between the monomer and the J-aggregates in the solution.

$$nM = J_{(n\text{-}mer)}$$

The concentration of J-aggregated monomers nC_J was calculated as $nC_J = C - C_M$, C_J being the particle concentration of J-aggregate 'n' was estimated from the mass action relation.

$$K_J = C_J/C_M^n$$

The In nC_J was plotted against In C_M and it gives a straight line of slope 'n'. The plots are shown in fig 5 where the value of n is 4.7 in Kcl and 4 in Na_2So_4 solutions. Using the values of n, K_j and ΔG_J were calculated as $5.52x\ 10^{12}$ dm^9/mo^{13} and $-7.2x10^{-4}$ Kcal/mol in Kcl solution respectively and $6.26x10^{12}dm^9$ / mo^3 and -7.3x10-4 Kcal / mol respectively in Na_2So_4 solution.

Estimation of 'n' from absorption line width was performed using the equation 'n' $= (W_M/W_J)^2$ where Wj is the longer wavelength half width at half height of J-band values of 'n' thus estimated are approximately 5.0 for Kcl solution and 4.0 for Na_2So_4 electrolytes. The value of n estimated from identical spectra by two independent methods are of the same order of magnitude. The strong tendency to form J-aggregation in presence of electrolytes thereby suggests that Dye I may be used efficiently in photography and in optical memory systems.

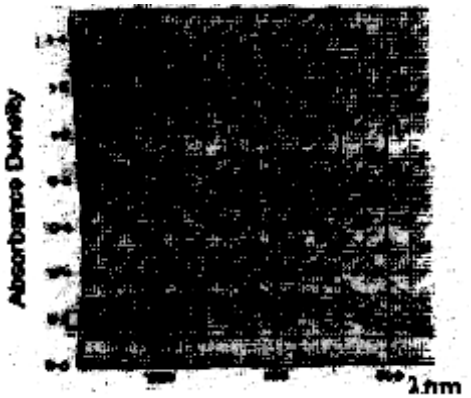


Fig. 1. Absorption spectrum of Dye I in aqeous methanol Dye concentration (mol) 1.2.5x10^{-6}, 2.5x10^{-6}, 3.75x10^{-6}, 4.1x10^{-5}, 5.25x10^{-5}

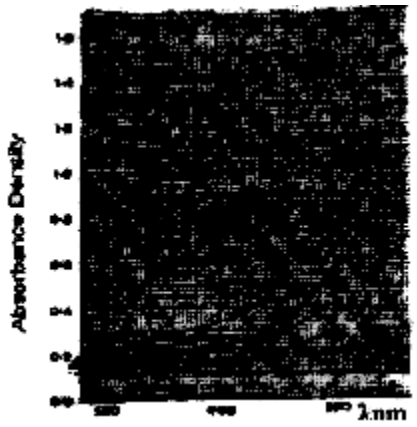


Fig. 2. J-aggregation absorption spectrum of Dye I in Kcl

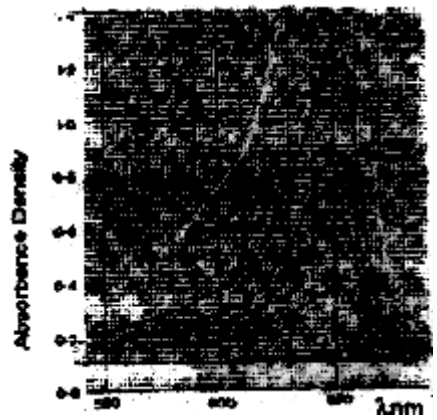


Fig. 3. J-aggregation absorption spectrum of Dye I in Na_2So_4

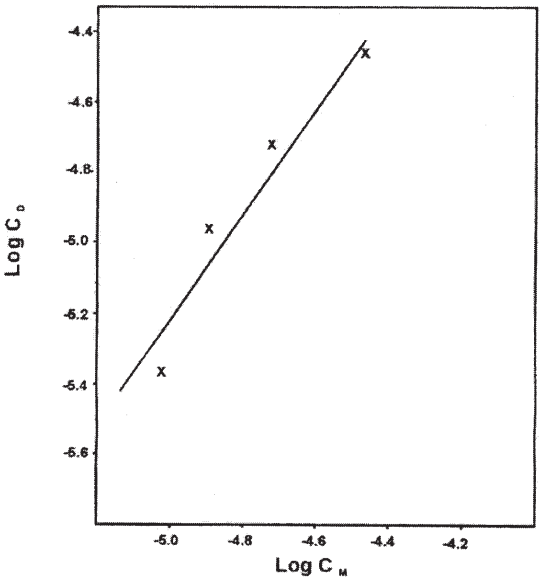


Fig. 4. Log C_M Versus Log C_D of Dye I

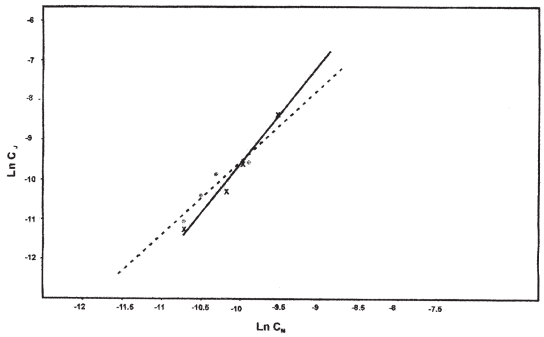
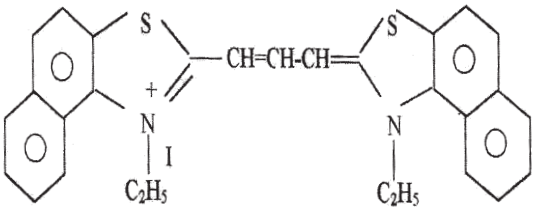


Fig. 5. Ln C_J Versus Ln C_M of Dye I

_____ In Kcl Solution
- - - - - - In Na_2So_4 Solution



Dye I

Further it was noted that on titrating the J-aggregated dye solution with methanol, the spectrum reveal stronger changes that the longest wavelength components (650nm) disappeared completely and the spectrum of the monomer, peaked at 574nm was obtained, indicating dissolution of the J-aggregates into dye monomers.

REFERENCES

1. Balzani, V. and Scandola, F. Supramolecular photochemistry, Ellies Horwood; chichester (1991).
2. Kuhn, H., *Pure Appl. Chem.,* **27**, 421 (1971).
3. Decher, G. and Hong, J.D. Ber. Bunsen-Ges. *Phys. Chem.,* **95,** 1430 (1991).
4. Von Berlepsch, H. Moher S. and Dahne I., *J. Phys. Chem.,* B **105,** 5689 (2001).
5. Wurthner, F. Thalacker, C. Diele S. and Tschierske c.
   C. *Chem. Eur. J.,* **7,** 2245 (2001).
6. Hu X. and Schulten, K. Physics Today **8,** 28 (1997).
7. Mc Dermott, G. Prince, S.M, and Issac N.W., Nature, **374,** 517 (1995).
8. Von. Berlepsch H. Kirstein S. and Bottcher C., Langmuir, **18,** 7699 (2002).
9. West, W. and Carroll B.H. in the theory of photographic process, 3rd ed. James T. H. Ed. Macmillan, New York, 233 (1966).
10. Ando E. Hibino J. Hashida and Morimoto K., Thin solid films *160,* 279 (1988).
11. Tanaka, T. and Matsubara T. J. Iimag Sci. and Tech. **87,** 585 (1993).
12. Tanaka T. and Matsubara T. J. Iimag Sci., and Tech. **39,** 373 (1998).
13. Boris, I. Shapiro, Alexandra yu. Uspenskaya and Valeria I. Avdeeva IS& T S 49th Annual Conference 99 (1996).
14. Makio S. Kanamaru N. and Tanaka J. Butt. Chem. Soc. Jpn, **53,** 3120 (1980).
15. Herz A.H. photographic sci. Eng., **18,** 323 (1974).