J-AGGREGATION OF CARBOCYANINE DYE AND THERMODYNAMIC PROPERTIES

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ABSTRACT

Apparently reversible and dissociation of small, metastable primary J-aggregate particles and dimeric particles of a phanchromatic carbocyanine dye I in moderately dilute aqueous methanol solutions containing electrolytes (KCl and Na₂SO₄) 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 materials¹. By control of the non covalent interactions, different extended supramolecular assemblies could be designed²-⁵. However beyond the field of material science, molecular aggregates also play a fundamental role in living matter, for example, in the processes of photosynthesis⁶, 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 systems⁷,⁸. 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 materials⁸ but also because of their potential applicability to multi frequency optical memory systems¹⁰. The existence of stable J- aggregates in aqueous solution is evidenced by light scattering and demonstrated by solution centrifugation and electron microscopy⁹,¹⁰. 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 systematically¹¹-¹⁴. 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-yldine)-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 10⁻⁶M, 5x10⁻⁶M and 7.5x10⁻⁶M. 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 εₘ value of 7.13x10³ dm³/mol.cm and the absorption line width Wₘ of free monomer we can use εₘ A and the following equation to calculate the monomeric, Cₘ, and dimeric concentration, Cₐ

\[ Cₐ = C - Cₘ \]

For each total dye concentration C, equilibrium free monomer concentration, Cₘ was determined from measured monomer band absorbance and εₘ. A plot of log Cₘ versus log Cₐ (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

\[ 2M \rightarrow D \]

Therefore Kₐ = Cₐ / Cₘ² was calculated as 1.112x10⁴ dm³/mol and the free energy ΔGₐ = -RTln Kₐ as -2.50x10⁻² Kcal/mol.

The electrolytes KCl and Na₂SO₄ 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.

\[ nM = J_{(n-mer)} \]

The concentration of J-aggregated monomers nCₐ was calculated as nCₐ = C - Cₘ , Cₐ being the particle concentration of J-aggregate ‘n’ was estimated from the mass action relation.

\[ Kₐ = Cₐ / Cₘ^n \]

The ln nCₐ was plotted against ln Cₘ 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 Na₂SO₄ solutions. Using the values of n, Kₐ and ΔGₐ were calculated as 5.52x10¹² dm⁹/mol¹⁰ and -7.2x10⁻⁴ Kcal/mol in KCl solution and 6.26x10¹²dm⁹ / mol and -7.3x10⁻⁴ Kcal / mol respectively in Na₂SO₄ solution.

Estimation of ‘n’ from absorption line width was performed using the equation ‘n’ = (Wₘ/Wₗ)² where Wₗ 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 Na₂SO₄ 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 aqueous 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 Na2SO4

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

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

Dye I
Further it was noted that on titrating the J-aggregated dye solution with methanol, the spectrum reveals 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.

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