

J-Aggregation Formation of Cyanine Dyes

Dr. K. A. Vijayalakshmi¹, R. Lavanya Dhevi²

¹Department of Physics, Sri Vasavi College, Erode-638316 Tamilnadu, India

²Department of Physics, Velalar college of Engineering and Technology, Thindal Erode-638316, Tamilnadu, India

Abstract: The aggregation of the red sensitizing cyanine dye (CY347B) in aqueous solution has been investigated using uv-visible spectroscopy (UV-Vis). The j-aggregates of the cyanine dye were formed upon addition of KCl to the dimers of the dye in solution. The appearance of the trimers in the uv-visible spectra suggests that the dye dimers are quantitatively converted to J-aggregates and equilibrium was reached. Using Benesi-Hildebrand kinetics, aggregation number 10 was calculated for the dye.

1. Introduction

J-Aggregates (or) S-Aggregates are dyes with a narrow absorption band that is shifted to longer wavelengths (or) lower frequencies with respect to the absorption band with a nearly resonant fluorescence. The shift of absorption band to longer wavelength is called Bathochromic shift [1]-[5]. The J and the S in the aggregate name denotes Edwin E Jelly and Gantner Scheibes in honour of their inventor.

The self association of dyes in solution (or) at the solid-liquid interface is a strong intermolecular vander waals-like attractive forces between the molecules [6]. The aggregates in solution exhibit distinct changes in the absorption band as compared to the monomeric species. From the spectral shifts, various aggregation patterns of the dyes in different media have been proposed. The Bathochromically shifted J-bands (J for jelly one of the first workers who investigated these shifts) of the aggregates have been explained in terms of molecular exciton coupling theory (ie) coupling of transition moments of the constituent dye molecules. The aggregates that exhibit J-band in their absorption spectrum are called J-aggregates.

Bathochromic shift is a change of spectral band position in the absorption, reflectance transmittance or emission spectrum of a molecule to a longer wave length (or) lower frequency. Bathochromic shifts are referred to as red shifts. Studies on J-aggregates resulted that these aggregates exist as a one-dimensional assembly in solution that could be in (a) brick work (b) ladder (c) staircase type. In the present work a red sensitizing cyanine dye (CY347B) shown in Fig(1) was chosen and its characteristic properties were studied.

It can also be found in various structural applications including planar and cylindrical aggregates exhibiting different optical and energy transfer properties[7]-[10]. It have wide applications in photonic devices such as optical switching, optical computing, and optical logic gate[11-13]. Aggregation of cyanine dyes have been induced by altering the concentration of the dye, temperature, concentration of added inorganic salts and bases[14]-[15]. In the paper presented here the formation of J-aggregates of cyanine dye have been reported and the kinetic aspects of the aggregation process were also discussed.

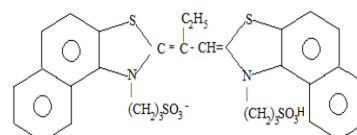


Figure 1: Structure of cyanine dye (CY 347 B)

2. Sample preparation and Experimental Work

0.01g of red sensitizing dye CY347B (Merck GR) was weighed accurately up to two decimals using digital chemical balance. The stock solution of the cyanine J-aggregate was prepared by dissolving 0.01g of the dye in 100ml of solution to obtain a concentration of 0.01M. Methanol was used in making the solution. 50 ml of stock solution was added with methanol to make 500 ml and to obtain a concentration of 0.001M. This prepared solution was labeled as "A". Another solution "B" of 500ml was prepared by taking 50ml of methanol and 450 ml of distilled water. Specimen solutions of various dye concentrations (D) were prepared by appropriate ratios of solution A and solution B.

The aggregate solution for each concentration was made by adding 0.5g of Potassium chloride (KCl) as electrolyte and named as D₁. The absorption spectra were measured for each concentration with the absorption spectrophotometer. The same procedure was repeated for Potassium sulphate (K₂SO₄) as electrolyte and labelled as dye solution (D₂).

3. Results and Discussions

Results and Discussions are subdivided into monomer absorption, aggregate absorption and calculations.

3.1 Monomer absorption for D₁ and D₂

The maximum absorbance of the monomer shown in Fig(2) for the dye D₁ occurs at 541nm where as for dye D₂ Fig(3) it occurs at 540 nm. The Beer-Lambert Law requires the absorbance of the monomer to increase with concentration, however the intensity of the blue shifted band increases with concentration. The lowest concentrated sample has an absorbance intensity 0.155 for D₁ and 0.131 for D₂, while the highest concentrated sample has an absorbance intensity of 0.242 for D₁ and 0.238 for D₂. The absorption of the monomer in this region of electromagnetic spectrum has

extended conjugation of π - electrons in the molecule which minimizes electron repulsion and the transition energy.

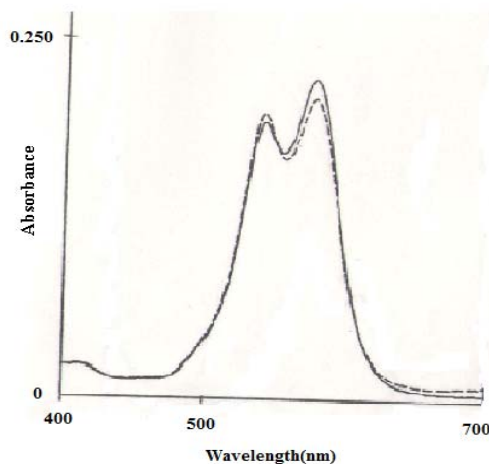
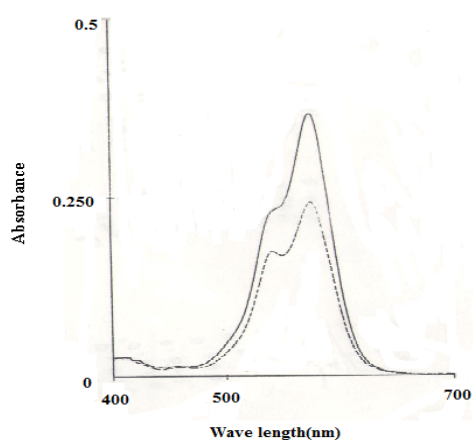
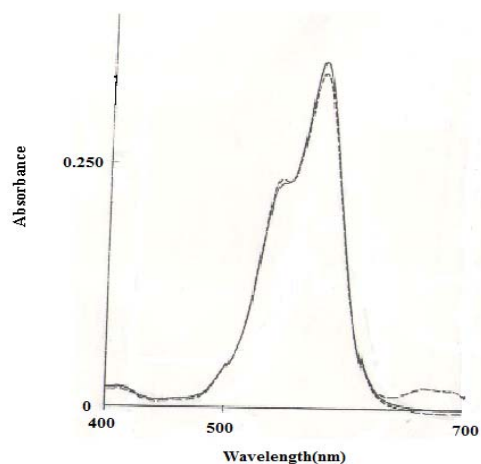
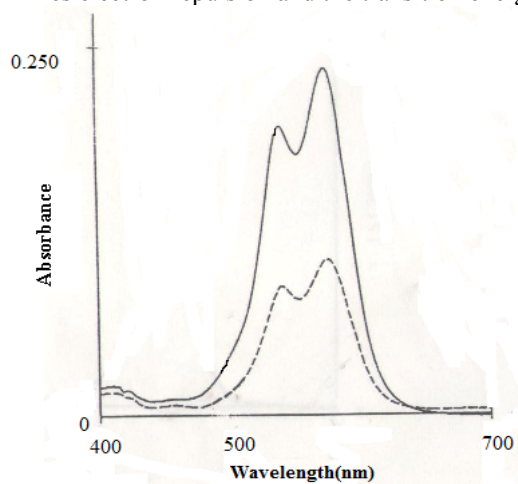


Figure 2: Monomer Absorption for D₁

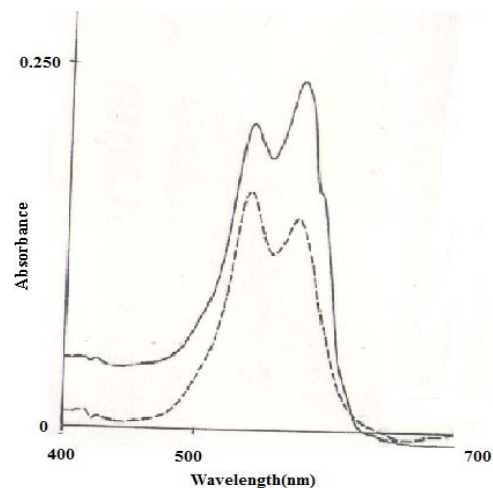
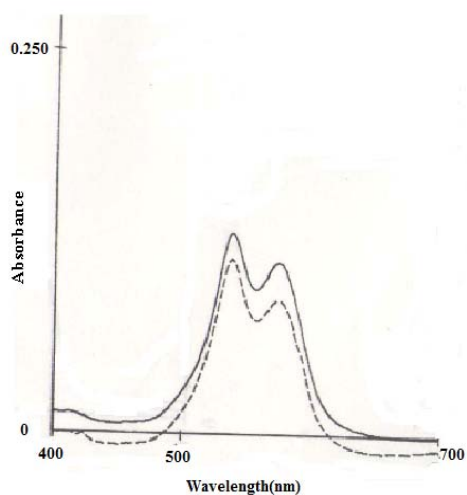


Figure 3: Monomer Absorption for D₂

3.2 Aggregate Absorption

The J-aggregate sample absorbs at $\lambda=593\text{nm}$ relative to the monomer .Hence the absorption has been Bathochromically shifted (or) red shifted as shown in Fig(4)[16]-[18].When Potassium Chloride (KCl) salt was added to monomer solution, it promotes J-aggregation by increasing dielectric constant, Consequently ,the electrostatic repulsion between dye ions is minimized and then aggregation is accelerated.[19]-[20].The molecules are bonded together by electrostatic forces with a chain like configuration. The

occurrence of the J-band confirms the formation of network super structures and complex fiber bundles.

When Potassium Sulphate (K₂SO₄) salt was added to monomer solution it does not promote J-aggregation. So it may not be a suitable electrolyte for photographic emulsions.

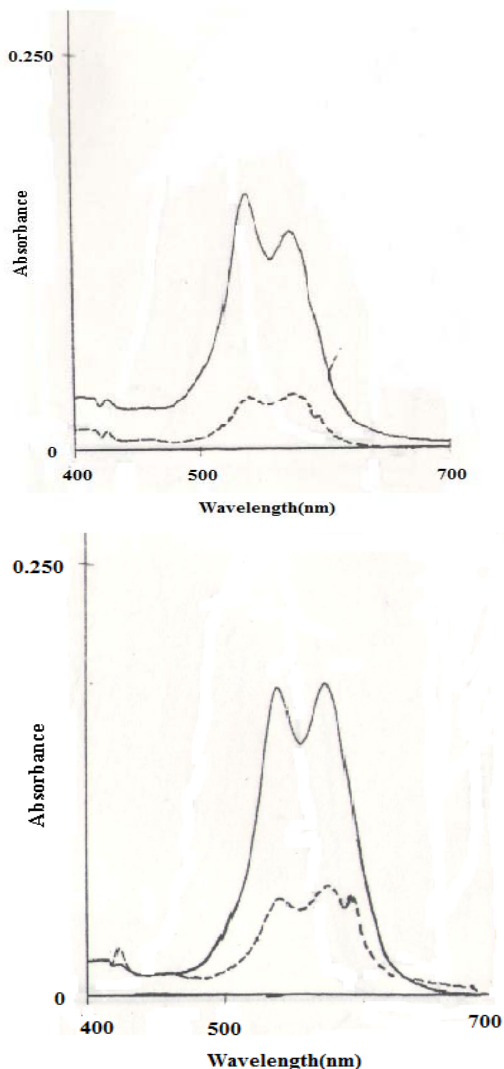


Figure 4: Aggregate Absorption

3.3 Calculations

The absorption spectrum of dye D₁ (Dye in KCl Electrolyte) at different concentrations in 10% aqueous methanol were compared with those of the dye in pure methanol. The absorption spectrum of pure methanol was for determining ϵ_m and the absorption line width W_m of free monomer ϵ_m was calculated using the formula

$$\epsilon_m = AC \tag{1}$$

where A is the absorbance of the monomer band and C is the concentration. We then use ϵ_m , A and the following equation to calculate Monomeric and Dimeric concentration

$$C_D = (C - C_M)/n \tag{2}$$

For each total dye concentration C equilibrium free monomer concentration C_M was determined from the measured monomer band absorbance (A) and ϵ_m

$$C_M = \epsilon_m/A \tag{3}$$

A graph is drawn between log C_D and log C_M which shows a straight line of slope n, indicating that there is an equilibrium between Monomer and Dimers in the solution which can be described as



Therefore

$$K_D = C_D/C_M^2 \tag{5}$$

The ΔG_D value was calculated according to thermodynamic equation

$$\Delta G_D = RT \ln K_D \tag{6}$$

The dye solutions in the presence of KCl electrolyte was studied. The electrolyte promotes the aggregate system organization. The concentration of J-aggregated monomers nC_J was calculated using the equation

$$nC_J = C - C_M \tag{7}$$

C_M being the particle concentration of J-aggregate.

The association number n can be determined from the absorption spectra of solutions of various dye concentrations using the mass action relation between the concentrations of free monomers (C_M) and J-aggregate particles. Once n is determined the association constant K_J is defined.

$$K_J = C_J/C_M^n \text{ (or) } l_n n C_J = n l_n C_M + l_n n C_J \tag{8}$$

When a graph $l_n n C_J$ was plotted against $n l_n C_M$ a straight of slope n was obtained. Using the value of 'n' K_J was calculated using the equation

$$n = (W_M/W_J^2) \tag{9}$$

Where W_M and W_J are the longer wavelength half widths at half height of the monomer and J band respectively.

From the values of K_J the ΔG_J value was obtained using the relation

$$\Delta G_J = RT \ln K_J \tag{10}$$

Similar study was performed for the dye D₂ (Dye in K₂SO₄ electrolyte)

3.3.1 Dye in KCl electrolyte

The absorption spectra of D₁ (Dye in KCl electrolyte) Fig (2) of different concentration in 10% aqueous methanol were compared with those of the dye in pure methanol Fig(5a). The peaks at 575nm and 540nm can be described to Monomer (M) and Dimer (D) band respectively. The absorption spectrum of Fig(2) was for determining ϵ_m and the absorption line width W_M of free monomer. ϵ_m value for the dye D₁ was 2.9458*10⁻³ dm³/mol.cm at 575nm.

The Monomeric and Dimeric concentrations for the dye D₁ was calculated using equations 2 and 3 and it was found to be C_M=1.7422*10⁻³g/mol and C_D=7.282*10⁻³ g/mol. A plot of log C_D and log C_M shows a straight line of slope approximately 2 as in Fig 6. Therefore K_D value obtained for dye D₁ was 2.6203 M⁻¹ using equation 5 and the ΔG_D value obtained was -1.250 KJ/mol using equation 6.

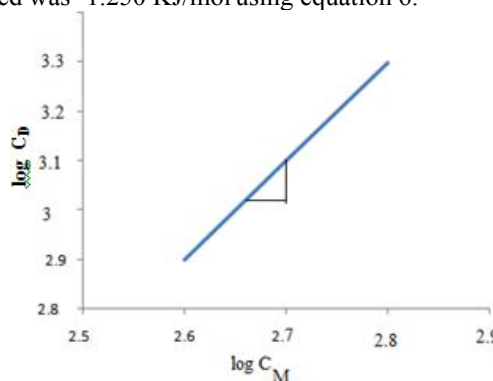


Figure 6: Plot of log C_D on log C_M

The dye solutions in the presence of KCl electrolyte have been studied. Fig 4 shows the aggregate spectra of dye D₁. It Exhibits the monomer peak at 578 nm and a predominant J band peak at 593 nm. The concentration of J-aggregate monomers nC_J was calculated using equation 7 and it was to be 1.4522×10^{-3} mol.

Estimation of 'n' from absorption line width was performed using the equation 9 and it was found to be 10. The K_J value can be calculated using equation 8 and it was found to be 4.0633×10^{-31} dm⁹/mol³. From the value of K_J the ΔG_J value can be calculated using equation 10 and it was to be 2.328 KJ/mol.

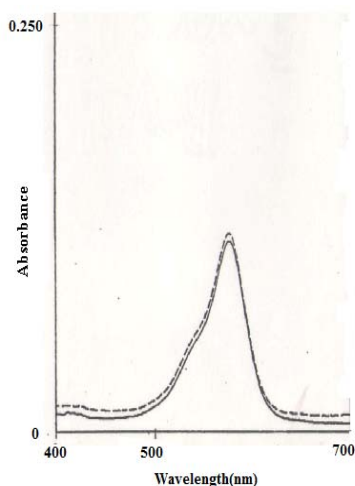
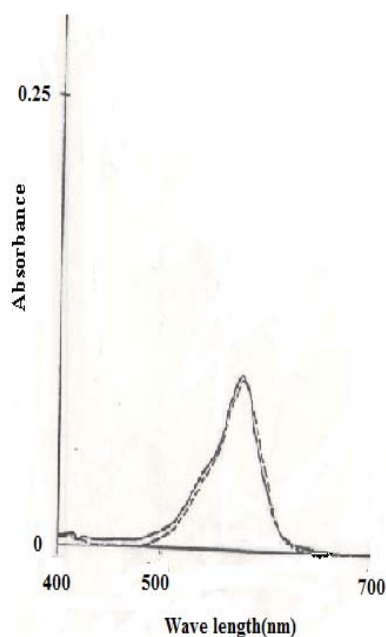


Figure 5(a) and 5(b) UV Spectrum in pure methanol solution for dye D₁ and D₂

3b) Dye in K₂SO₄ electrolyte:

The absorption spectra for the dye D₂ (Dye in K₂SO₄ electrolyte) was shown in Fig 3. The spectrum of D₂ at different concentrations in 10% aqueous methanol were compared with those of the dye in pure methanol solution Fig 5(b). The peaks at 575 nm and 540 nm can be described as Monomer (M) and Dimer (D) band respectively. The absorption spectrum Fig (3) was used for the determination of ϵ_M . The Monomeric and Dimeric concentrations for the dye D₂ was found to be $C_M = 1.568 \times 10^{-3}$ g/mol and $C_D = 6.4108 \times 10^{-4}$ g/mol. A plot of $\log C_D$ vs $\log C_M$ shows a

straight line of slope approximately 2 as in Fig 7. Therefore K_D value obtained for dye D₂ was 2.833×10^{-2} dm³/mol using equation 5 and ΔG_D value obtained was 1.2675 KJ/mol.

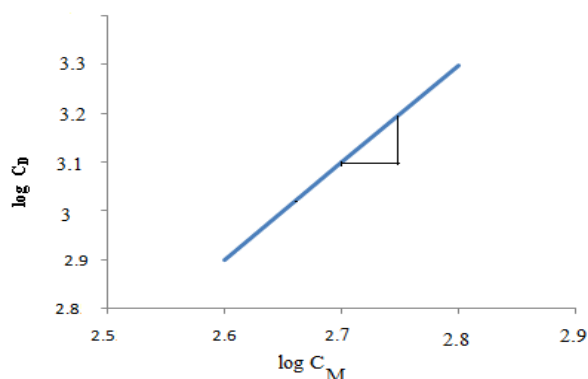


Figure 7: Plot of $\log C_D$ on $\log C_M$

4. Conclusion

The formation of J-aggregate is enhanced by the addition of KCl to solution of the (monomer) not by the K₂SO₄. The aggregate spectra show an intense peak at 593 nm. The spectra shows an equilibrium is established between aggregate and monomer. From the data obtained, we calculate the aggregation number, equilibrium constant and the Gibbs free energy of the aggregation. The calculated number of 10 could be increased by adjusting substituent's on the heterocyclic rings of the J-aggregate which improves on spectral properties and for applications in high technology fields.

Reference

- [1] G. Scheibe, "Über die Veränderlichkeit der Absorptionsspektren in Lösungen und die Nebenvalenzen als ihre Ursache," *Angewandte Chemie*, vol. 50, no. 11, pp. 50–219, 1937
- [2] G. Scheibe, L. Kandler, H. Ecker, *Naturwissenschaften* 1937, 25, 75;
- [3] G. Scheibe, "Über die Veränderlichkeit des Absorptionsspektrums einiger Sensibilisierungsfarbstoffe und deren Ursache," *Angewandte Chemie*, vol. 49, p. 563, 1936.
- [4] E. E. Jelley, "Spectral absorption and fluorescence of dyes in the molecular state," *Nature (London)*, vol. 138, p. 1009, 1936. E. E. Jelley, *Nature* 1936, 138, 1009-1010
- [5] E. E. Jelley, "Molecular, nematic and crystal states of 1,1-Diethyl-c-cyaninechloride," *Nature (London)*, vol. 139, p. 631, 1937.
- [6] Cyanines during the 1990s: A Review, *Chem. Rev.* 2000, 100, 1973-2011
- [7] F. Wurthner, T. E. Kaise, and C. R. Saha-Moller, "J-Aggregates: from serendipitous discovery to supramolecular engineering of functional dye materials" *Angew. che. Int. Ed.* 50, 3376, 2011
- [8] A. Einfeld, R. Kniprath and J. S. Briggs, "Theory of the absorption and circular dichroism spectra of helical molecular aggregates", *Journal of chemical physics*. 126, 104904, 2007.
- [9] L. D. Bakalis and J. Knoester, "Optical properties of one-dimensional exciton systems: Beyond the Heitler-London approximation" *Journal of chemical physics*. 106, 6964, 1997

- [10] A.Pugzlys,R.Augulis,P.H.M.VanLoosdrecht,C.Didraga, V.A.Malyshev and J.Knoester, " Temperature-Dependent Relaxation of Excitons in Tubular Molecular Aggregates: Fluorescence Decay and Stokes Shift" *Journal of Physical Chemistry*.B110,20268,2006
- [11] K.Ohta,M.Yang,G.R.Fleming,"Ultrafast exciton dynamics of J-Aggregates in room temperature solution studied by third-order nonlinear optical spectroscopy and numerical simulation based on exciton theory", *Journal of Chemical Physics*,115:7609-7621,2001[DOI]
- [12] R.V.Markov, A.I.Plekhanov,V.V.Shelkovnikov,et.al "Nonlinear optical properties of one-dimensional organic molecular aggregates in nanometer films." *Microelectronic Engineering*,69:528-531, [DOI]2003
- [13] A.V.Vannikov,A.D.Grishina,B.I.Shapiro,et al "Photoelectric,nonlinear optical and photorefractive properties of polyimide doped with J-aggregates of cyanine dye".*Chemical Physics*,287:261-271[DOI]2003
- [14] I.A.Struganova,L.Hyunsoo and M.A.Simone,"The Influence of Inorganic salts and Bases on the formation of the J-band in the Absorption and Fluorescence spectra of the Diluted Aqueous Solutions of TDBC". *J.Phys.Chem.B*,106,11047-11050,2002.
- [15] I.A.Struganova" Dynamics of formation of 1,1'-Diethyl-2,2'-Cyanine Iodide J-Aggregates in Solution", *J.Phys.Chem.A*,104,9670-9674,2000
- [16] A.K.Chibisov,H.Gorner,T.D.Slavnova,"Kinetics of salt Induced J-Aggregation of an anionic thiocarbocyanine dye in aqueous solution" *Chemical Physics Letter* 390,240,2004.
- [17] T.D.Slavnova A.K.Chibisov,H.Gorner," Kinetics of Salt-Induced J-aggregation of Cyanine Dyes" *Journal of Physical Chemistry.A* 109, 4758, 2005
- [18] H.Gorner, A.K.Chibisov, T.D.Slavnova , *Journal of Physical Chemistry B* "Kinetics of J-Aggregation of Cyanine Dyes in the Presence of Gelatin" 110,3917,2006
- [19] A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, and G. B. Behera, "Cyanines during the 1990s: a review," *Chemical Reviews*, vol. 100, no. 6, pp. 1973–2011, 2000.
- [20] M.Liu,A.Kira, "Fabrication of J aggregate Films in synthetic polyanion matrix and their chemochromism", Liua, M.; Kirab, A., *Thin Solid Films*, 359,104,2000.

aggregation formation and the absence of trimer peak in dye D₂(Dye in K₂SO₄ electrolyte) indicates that it is not be a suitable electrolyte for photographic emulsion formation because of the presence of sulphate ions.

Reference

- [1] Berriman R.W and Gilman, P.B, Jr.preprint papers, society of photographic scientists and engineers. International Symposium on the physics of the silver halide crystal.

Author Profile



R. Lavanya Dhevi received the M.Sc and M.Phil degrees in Physics and presently she is pursuing her Ph.D in plasma physics. She is presently working as Asst. Professor in the Department of Physics, Velalar College of Engineering and Technology affiliated to Anna University, Chennai. She had presented the paper in National conference.

Study of aggregation of cyanine dyes in solution can help us to understand the mechanism of photographic spectral sensitization of the dyes in the silver halide emulsions. The aggregate properties including the thermodynamic of the red sensitizing dyes have been studied thoroughly and systematically. Thus we conclude that this thermodynamic property is J-aggregation of dyes. The presence of trimer peak in dye D₁(Dye in KCl electrolyte) indicates the J-