

J-Aggregates of Cyanine Dyes in Aqueous Solution of Polymers: A Quantitative Study

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ABSTRACT

The effect of polyvinylsulfate (PVS) on the spectroscopy of the cyanine dye, 1,1'-diethyl-2,2'-cyanine iodide (PIC), has been investigated using UV-vis spectroscopy. J-aggregates of the PIC dye were formed upon addition of PVS to the monomers of the dye in solution. The appearance of only one isosbestic point in the UV-vis spectra suggests that the dye monomers are quantitatively converted to J-aggregates and equilibrium was reached. Using Benesi-Hildebrand kinetics, aggregation number of 4 was calculated for the dye. In addition, a 1:2 mole ratio of PIC/PVS was calculated at the maximum capacity of the polymer.

I. INTRODUCTION

Recently, organized film assemblies and nanocomposites of functionalized molecules have attracted the attention of several researchers due to their potential applications in nanotechnology, photoelectric cells, molecular electronic elements and non-linear optical devices. The self-assembly of cyanine dyes in different media has been recognized for several years [1-4]. It is well known that these dyes form J-aggregates through self-assembly in aqueous solutions and on surfaces like silver bromide crystals. Different methods have been employed to induce the aggregation of cyanine dyes such as altering the concentration of the dye, temperature, concentration of added inorganic salts and bases [5,6]. Shklyarevskiy [7] proposed the use of a high magnetic field to induce the alignment of J-aggregates from the monomers. This study focused on the self-assembly of cyanine dyes on charged surfaces in aqueous solutions and on substrates. The intermolecular self-association of PIC (Figure 1) in aqueous solution was induced by the presence of a charged polymer or nanoparticles of clay in the solution. In this paper we report the formation of J-

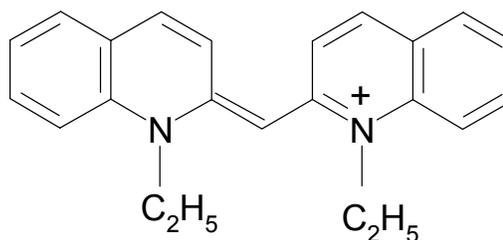


Figure 1. Structure of 1,1'-diethyl-2,2'-cyanine dye

aggregates of PIC on polyvinylsulfate in aqueous solution. Furthermore, the kinetic aspects of the aggregation process were also discussed.

II. EXPERIMENTAL SECTION

A 2.20×10^{-2} mM aqueous solution of PIC was prepared as a stock solution and a more diluted solution of a concentration of 1.76×10^{-3} mM was prepared from the stock solution by dilution as needed. Also an aqueous solution of PVS potassium salt of 0.10 g in 50 mL (2.0 mg/mL) in de-ionized water was prepared fresh before use. Spectrophotometer from Ocean Optics (model CHEM 2000 UV-VIS) was used to

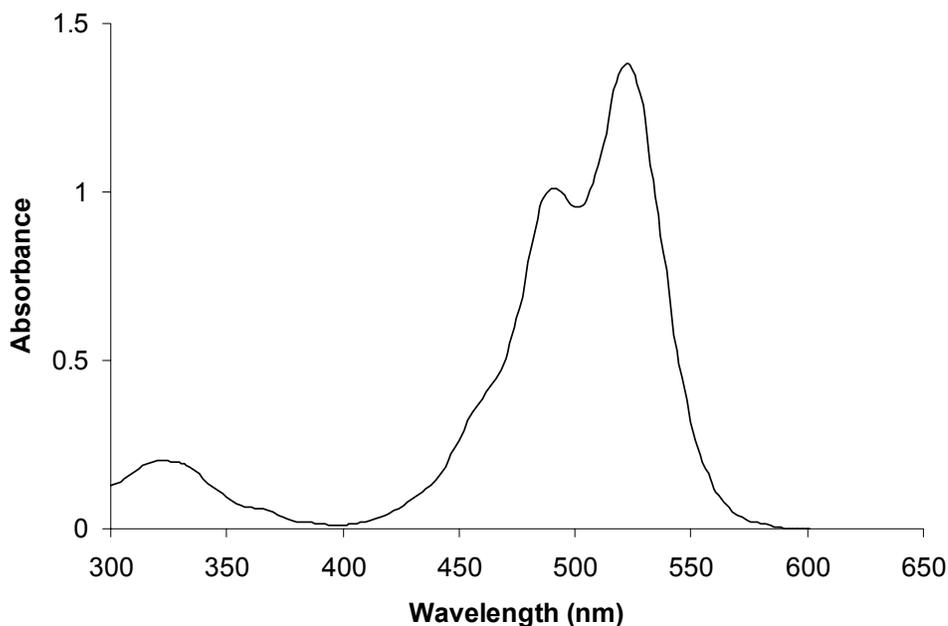


Figure 2. Absorbance of PIC (1.76×10^{-3} mM) in aqueous solution.

measure the absorbance of the dye in solution. The polymer solution was added in increments of $15 \mu\text{L}$ to a 2.0 mL of the dye solution in a cuvette. The solution was well mixed by shaking the cuvette and the absorbance of the dye was recorded immediately. The procedure continued until no further change in the absorbance of the dye was noticed.

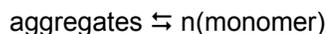
III. RESULTS AND DISCUSSION

The absorbance of the dye in aqueous solution is shown in Figure 2. Clearly, the spectrum indicates that the absorbance of the monomer (large band) occurs at 523 nm . After the addition of $5 \mu\text{L}$ of the PVS solution to 2 mL of the dye solution in the cuvette, a small but significant shoulder peak seems to appear at 572 nm in the absorption spectrum of the dye (Figure 3). This red shifted peak corresponds to the absorption of the J-aggregate of the dye.

After the formation of the aggregates and the J-band became evident, the polymer was added to the cyanine dye solution in the cuvette in increments of $15 \mu\text{L}$ until no further growth in the J-band was observed. During the addition of the

polymer solution, the absorbance of the dye monomers continued to decrease while the absorbance of the J-aggregates continued to grow as shown from Figure 4.

After about $105 \mu\text{L}$ of the PVS was added to the dye solution, no further change in the absorbance intensity of either the monomers or the aggregates occurred, which indicates the reach of the saturation point where every accessible exchanging site on the polymer has been occupied by a dye molecule (Figures 4 and 5). The appearance of only one isosbestic point in the UV-vis spectra suggests that when an aqueous solution of PIC is treated with a PVS solution, the dye monomers are converted to J-aggregates and equilibrium is reached, i.e.,



$$K = \frac{[\text{monomer}]^n}{[\text{aggregates}]} \quad (1)$$

and

$$\ln(K) = n \ln([\text{mon}]) - \ln([\text{agg}]) \quad (2)$$

where K is the equilibrium constant. Equation (2) demonstrates the relationship between the concentrations of the monomer

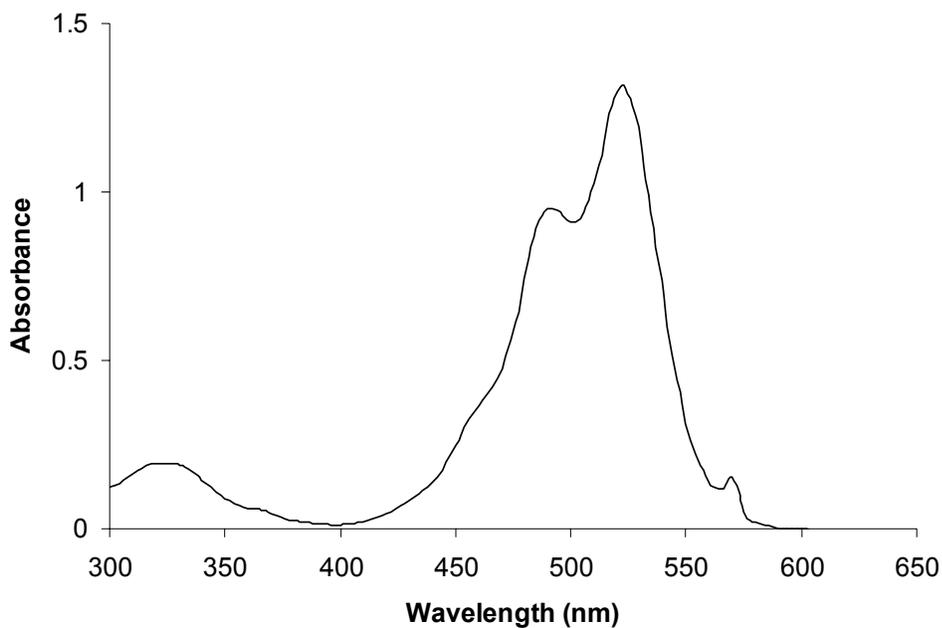


Figure 3. Absorbance of PIC after the addition of 5 μL of PVS Solution.

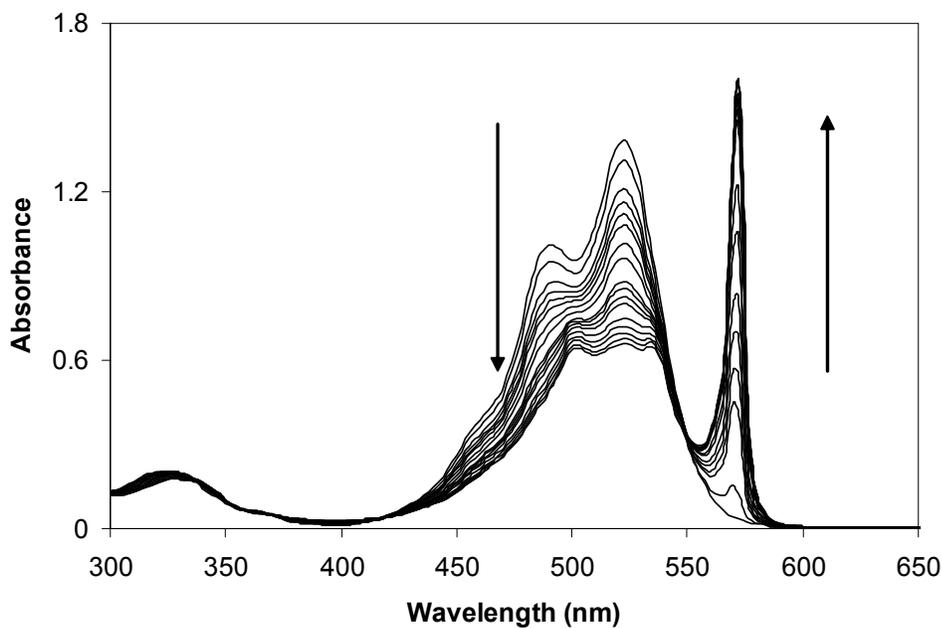


Figure 4. Absorbance of PIC after addition of 15 μL of PVS solution incrementally.

and the aggregate in solution using the aggregation number, n .

According to Benesi-Hildebrand kinetics, the above equilibrium can be

described by the absorbance of the aggregates and the monomers, Equation (3), where A_{agg} and A_{mono} are the

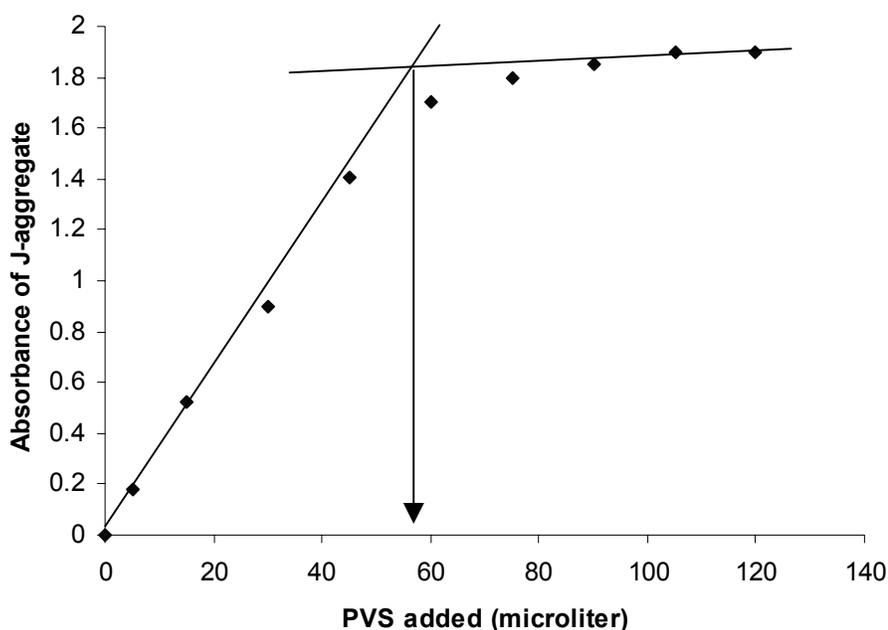


Figure 5. Absorbance of J-Aggregate as a function of the volume of PVS added.

absorbance of the aggregates and the monomers respectively, under equilibrium.

$$\ln(A_{agg}) = n \ln(A_{mon}) + \text{constant} \quad (3)$$

The plot of $\ln(A_{agg})$ against $\ln(A_{mon})$ yields a straight line with a slope of 4, representing the aggregation number n of PIC in PVS solution.

Using the molar mass of 146 g/mol for the repeating unit of PVS, the concentration of the polymer was calculated to be 6.85×10^{-3} mol of repeating units/gram of polymer. This information together with the calculated concentrations of PVS and the dye molar concentration in the cuvette, was used to calculate a molar ratio PIC/PVS of 48%, at saturation. This corresponds to a 1:2 mole ratio of the aggregated dye to the repeating units of the polymer. Taking into consideration the size of the dye molecule (surface area of 60 \AA^2) and the calculated PIC/PVS mole ratio, it can be proposed that the dye molecules are occupying every other unit on the polymer. Also, because of the known molecular geometry of the aggregates and the folding nature of the PVS, we were not surprised that the 1:2 mole ratio was obtained. In the absence of

any reported data on the stoichiometry of the aggregation process in PVS solutions, this result remains an area for future research that will focus on the characteristics of the aggregates and its relation to our findings.

An attempt was made to add the dye solution to the PVS in the cuvette while keeping the concentration of the PVS below the saturation level. This resulted in no aggregate formation which could be attributed to the low concentration ratio $[\text{dye}]/[\text{PVS}]$. At low concentration ratio, the dye molecules will adsorb randomly at different parts of the PVS, and not necessarily close enough to each other in order for aggregate formation.

CONCLUSION

J-aggregates of the PIC dye were obtained upon addition of PVS to the monomers of the dye in aqueous solutions. The results suggest that the dye monomers are quantitatively converted to J-aggregates and a 1:2 mole ratio of PIC/PVS was obtained at the maximum capacity of the polymer.

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