

# Studies in Interaction Between Polyvinyl Pyrrolidone and Stilbene Fluorescent Compounds II. Interaction with Mixture of Compounds

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## Synopsis

Interaction between polyvinyl pyrrolidone (PVP) of different molecular weight and aqueous solutions of mixture of two stilbene type fluorescent compounds, which interact with each other, has been examined from the results of fluoremetric and UV absorbance measurements. Results indicate that combination of these compounds results in formation of a complex with reduced fluorescence characteristics. Addition of PVP to this complex brings about dissociation, followed by interaction of each component with PVP and subsequent formation of a different type of complex.

## INTRODUCTION

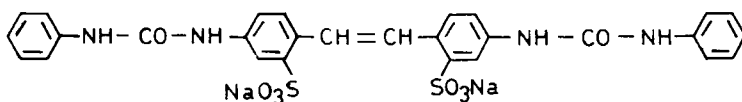
The presence of certain compounds, such as alcohols, pyridine, or nonionic polyethylene oxide condensates, has been found to prevent interaction between specific dyes, and the action of nonionic surfactants on the mixture of dyes is supposed to be one of deflocculation of the complex formed between the dyes followed by formation of a complex between dye and surface-active agent.<sup>1-3</sup> However, hardly any information is available on the effect of the addition of polymeric compounds on the interaction between dyes or fluorescent compounds. In Part I of this series,<sup>4</sup> interaction between polyvinyl pyrrolidone (PVP) and two stilbene-type fluorescent compounds of different chemical constitutions has been examined from fluoremetric and ultraviolet (UV) absorbance spectrophotometric studies. It has been shown that the trans form of the stilbene compounds interact preferentially with PVP to produce a complex having different fluorescence and UV absorbance characteristics. At higher concentrations of PVP, the cis form of the two compounds also interacts with PVP and a different type of complex results. In the present study, the effect of addition of PVP on the interaction of two stilbene-type fluorescent compounds, which interact with each other, has been examined from fluoremetric and UV absorbance spectrophotometric studies and the different types of complex formed as a result of such addition have been analyzed.

## EXPERIMENTAL

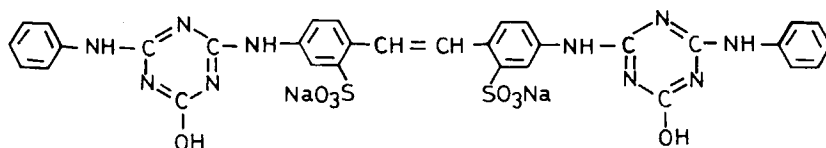
PVP having molecular weights of 10,000, 38,000, and 750,000 was obtained from GAF Corporation (United States), and PVP of molecular weight

47,000 was obtained from Calico Chemicals and Plastic Division (India). Molecular weight was determined from viscometric measurements at a temperature of 30°C using  $K$  and  $\alpha$  values of  $1.4 \times 10^{-4}$  and 0.70, respectively, as reported by Scholtan<sup>5</sup> for converting intrinsic viscosity to viscosity average molecular weight.

CI Fluorescent Brightener 30 and Fluorescent Brightener 32 with the following constitutions were selected as the stilbene types of fluorescent compounds.



C.I. FLOURESCENT BRIGHTENER 30



C.I. FLUORESCENT BRIGHTENER 32

The compounds were first dissolved in DMF followed by precipitation with acetone to remove inorganic impurities present. In case of triazine type of Brightener 32, the triazine impurities were removed by extraction with toluene according to the method suggested by Weller.<sup>6</sup> Purity of the compounds was checked chromatographically. Absorbance spectra of the aqueous solutions of the compound containing PVP were obtained on Hitachi model 200-20 spectrophotometer with 1 cm cell while 90° emission and excitation spectra were recorded on Aminco Bowman spectrofluorometer with 1 cm cell. For the measurement of emission spectra, excitation wavelength was kept at 370 nm for CI Fluorescent Brightener 30 and 376 nm for Fluorescent Brightener 32, while for excitation spectra, emission wavelength was kept at 410 nm for CI Fluorescent Brightener 30 and 430 nm for Fluorescent Brightener 32.

Two sets of experiments were conducted. In one case, the two fluorescent compounds were mixed together in equimolar proportion ( $0.25 \times 10^{-4}$  mol/L) and the complex was allowed to form completely. Subsequently, to this mixture was added different quantities of PVP (0.01–10 g/L) until no change in the fluorescence intensity or UV absorbance was observed. In the other case, each fluorescent compound was first mixed with PVP at a specific concentration (concentration beyond which there was no further change in fluorescence or UV absorbance at longer wavelengths) and then the two were mixed together followed by the measurement of fluorescence intensity as well as UV absorbance.

## RESULTS AND DISCUSSION

CI Fluorescent Brightener 30 and Fluorescent Brightener 32 are mixed in equimolar proportion, and both fluorescence intensity as well as absorb-

ance in UV region of the individual compounds and the mixture are recorded (Figs. 1 and 2). The mixture shows three absorbance bands at 240, 280, and 340 nm, which are the absorbance bands noticed in the case of the two components, 240 and 340 nm for CI Fluorescent Brightener 30 and 280 and 350 nm for Fluorescent Brightener 32. Both emission as well as UV absorbance spectra of the mixture are different from the additive spectra of the compounds when present individually. This goes to show that interaction between the two compounds does take place in the aqueous solution under the conditions studied and there is a quenching of fluorescence on mixing the two compounds.

The formation of the complex between the two stilbene compounds studied appears to be due to superposition of the two linear molecules, which makes very close approach of the molecules possible. Such types of complex have been found to take place when specific disazo dyes interact with each other.<sup>1,2,7</sup>

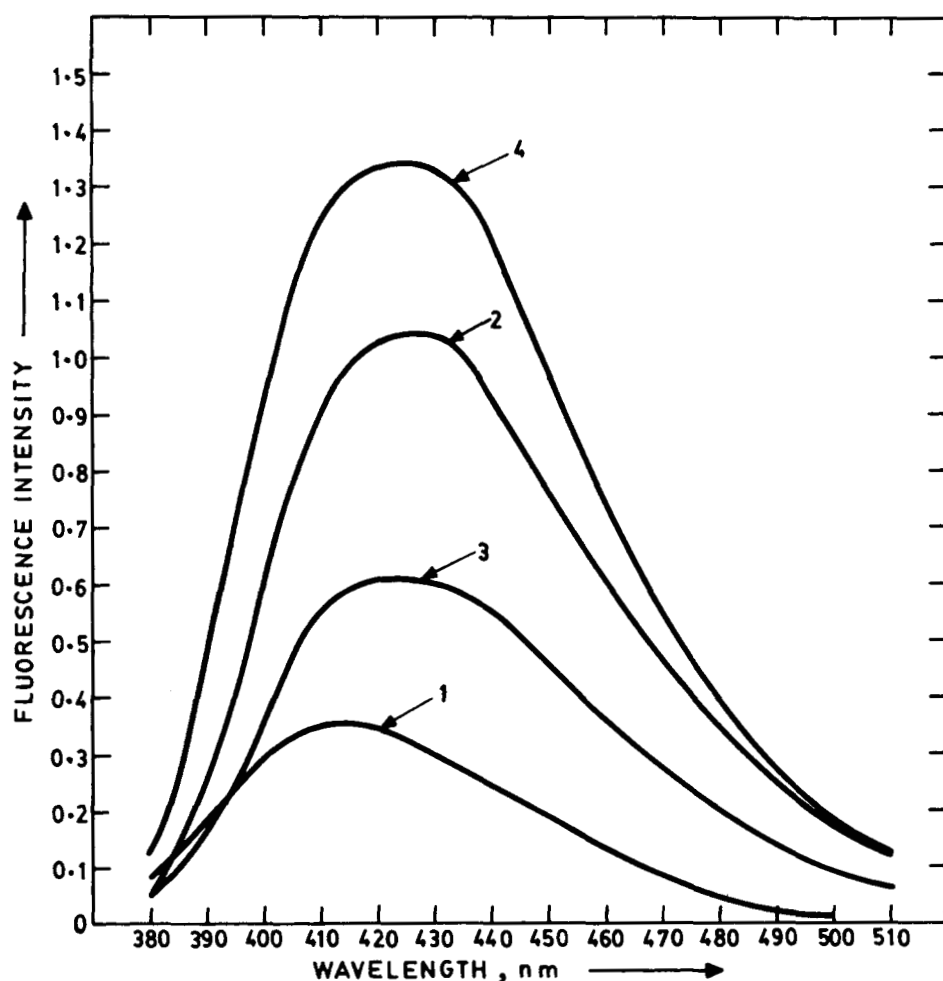


Fig. 1. Fluorescence spectra of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32: (1) Brightener 30 ( $0.25 \times 10^{-4}$  mol/L), (2) Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (3) mixture of Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) + Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (4) additive spectra of 1 and 2.

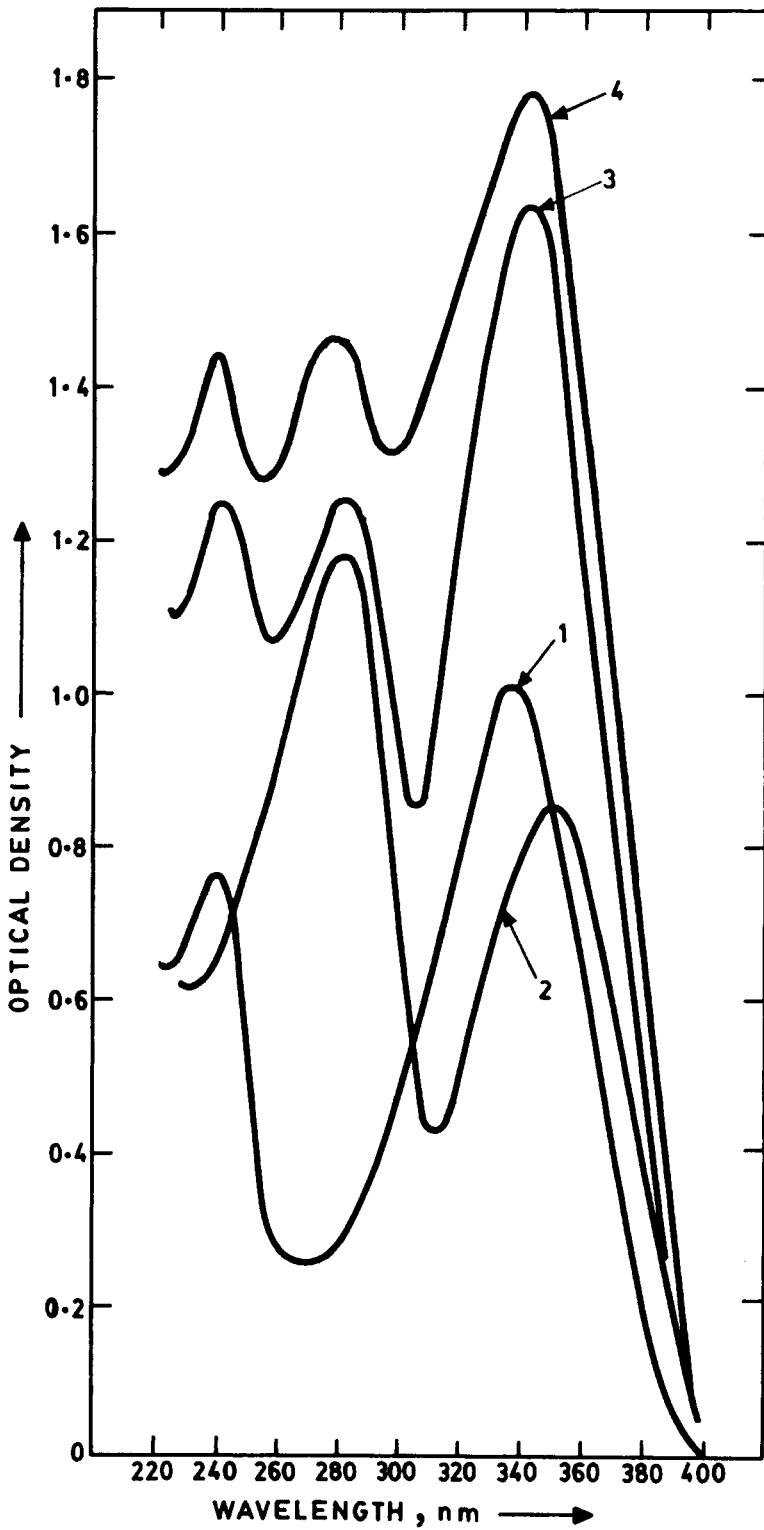


Fig. 2. Absorbance spectra of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32: (1) Brightener 30 ( $0.25 \times 10^{-4}$  mol/L), (2) Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (3) mixture of Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) + Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (4) additive spectra of 1 and 2.

The type of bonding during such interaction appears to be the nonpolar van der Waals forces, and it has been observed that the forces operative during such interaction are very similar to those that operate during aggregation of individual dyes as well as those binding these dyes to cellulosic fibers.

When PVP is added progressively to the mixture of the two compounds, it is found that fluorescence intensity is increased; it reaches a value higher than the value for each of the individual component present in the mixture (Fig. 3). The changes in fluorescence intensity are real, not an artifact, as observed from the fact that the values obtained on repeated experiments were very similar and, also, there was visual indication of a substantial increase in the fluorescence intensity as a result of PVP addition. Furthermore, UV absorbance at longer wavelengths is increased on progressive addition of PVP and there is a shift in  $\lambda_{\max}$  to longer wavelengths (Fig. 4). Such an increase takes place up to a concentration of PVP beyond which there is no further change in fluorescence intensity. As the UV absorbance is very high, self-filtering may occur. However, this possibility is not likely because PVP does not show absorbance in the region studied (Fig. 4) and the mixture without PVP gave an optical density of about 1.6, which increased to about 1.8 on addition of PVP, the concentration of the fluorescent compounds remaining constant. If filtering effects were to take place they would be the same for the mixture of fluorescent brightener without and with PVP. Thus, there is little doubt that the changes observed on addition of PVP are real, not due to the filtering effect.

The concentration of PVP (0.3 g/L) beyond which fluorescence intensity does not increase is identical with that beyond which absorbance at longer wavelengths also ceases to increase. Up to this specific stage of PVP addition, absorbance by the mixture at shorter wavelengths (240 and 280 nm) in the UV region does not change appreciably, but on further addition of PVP, there is a rapid increase in the absorbance at these wavelengths, a behavior similar to that observed for individual compound, as shown in Part I.<sup>4</sup>

In the case in which the two fluorescent compounds are first complexed with an optimum concentration of PVP (concentration beyond which there is no change in fluorescence or UV absorbance at longer wavelengths) and the two complexes are then mixed together, the resulting complex shows considerable quenching of fluorescence intensity and also UV absorbance is different from that of the sum of the absorbance by individual compound-PVP complexes (Figs. 5 and 6).

Although no definite information regarding the nature of interaction between stilbene compounds and PVP is available, two types of bonding that are likely to take place are the following, depending on the conditions during interaction:

1. Interaction between the amide group in the pyrrolidone ring of PVP and the aromatic system of the compound
2. Interaction between the aliphatic chain (methylene groups) of PVP molecule and the aromatic system in the compound, with induction forces and/or hydrophobic bonding being operative

The two stilbene types of compounds can assume a flat configuration that will result in maximum interaction with the paraffin chain of PVP. PVP has a fairly stiff polyvinyl chain with bulky substituents, with the result

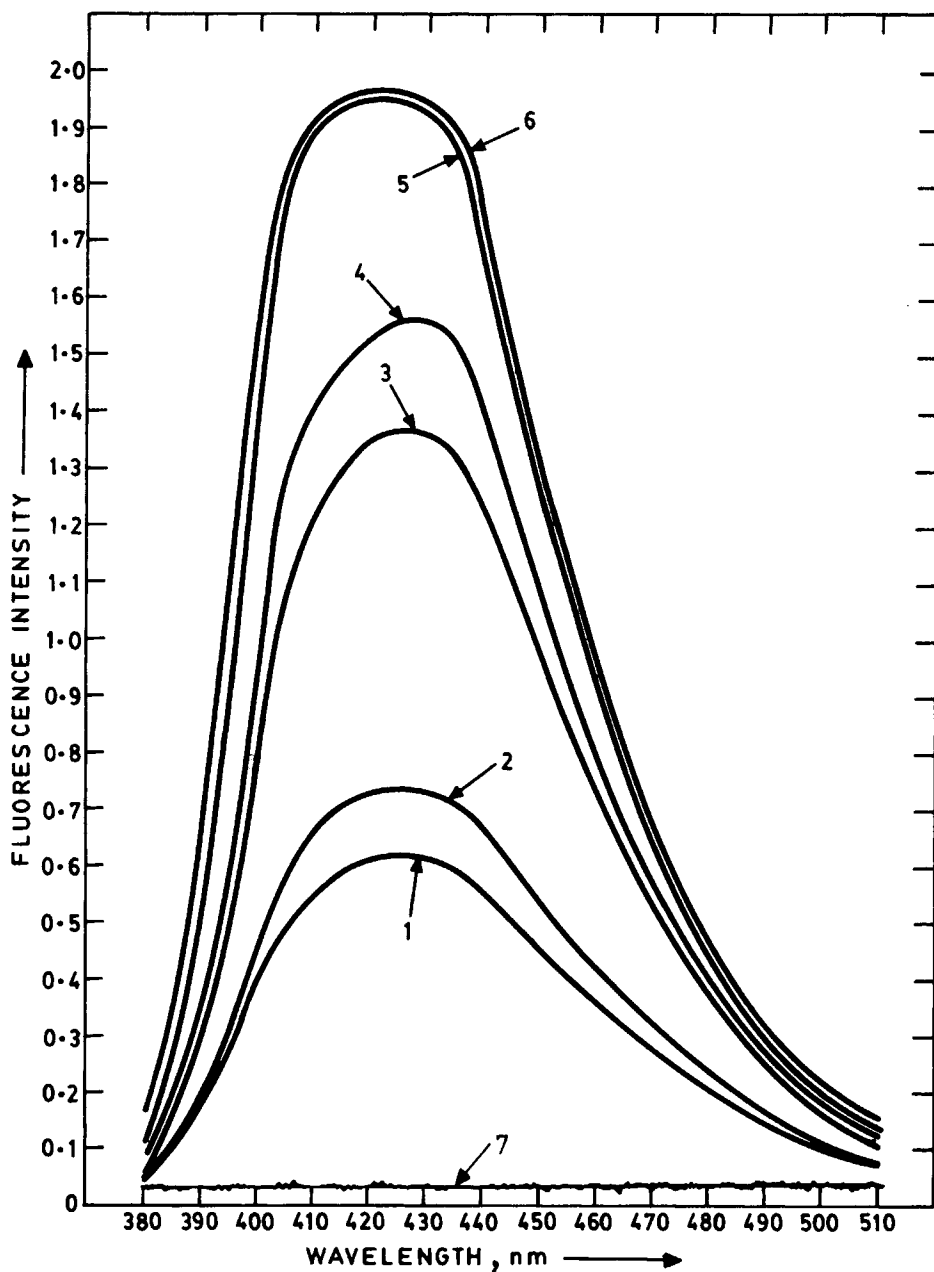


Fig. 3. Fluorescence spectra of the mixture of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32 in the presence of PVP: (1) mixture of Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) and Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (2) 1 + PVP (0.01 g/L), (3) 1 + PVP (0.05 g/L), (4) 1 + PVP (0.1 g/L), (5) 1 + PVP (0.3 g/L), (6) 1 + PVP (10.0 g/L), (7) PVP alone.

that much rotation around C—C bonds is not possible. As PVP molecule does not carry any ionizable groups at neutral pH, the binding forces are mainly due to intermolecular attraction. This is substantiated by the fact that the values of free energy change  $\Delta F$  ( $-7.5$  to  $-10.9$  kJ/mol) obtained for such interactions are quite low.<sup>4</sup> It can be presumed that the stilbene

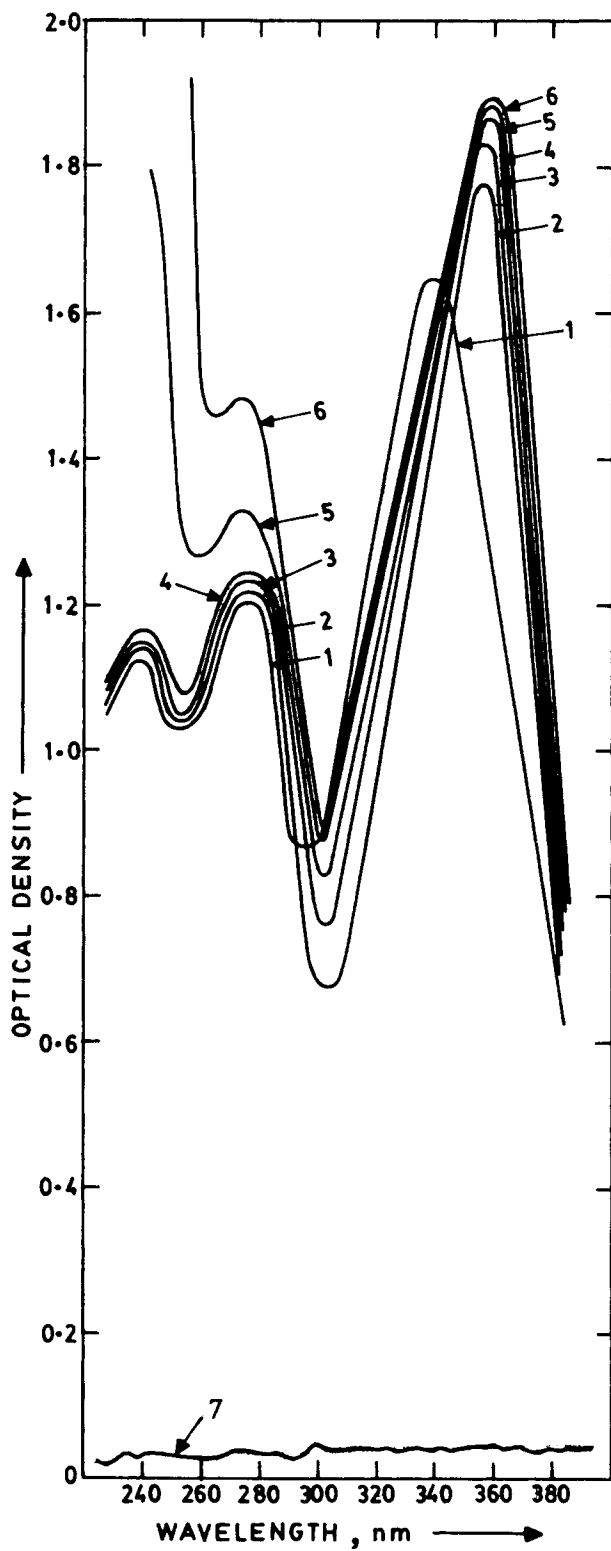


Fig. 4. Absorbance spectra of the mixture of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32 in the presence of PVP: (1) mixture of Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) and Brightener 32 ( $0.25 \times 10^{-4}$  mol/L), (2) 1 + PVP ( $0.05$  g/L), (3) 1 + PVP ( $0.1$  g/L), (4) 1 + PVP ( $0.3$  g/L), (5) 1 + PVP ( $5.0$  g/L), (6) 1 + PVP ( $10.0$  g/L), (7) PVP alone.

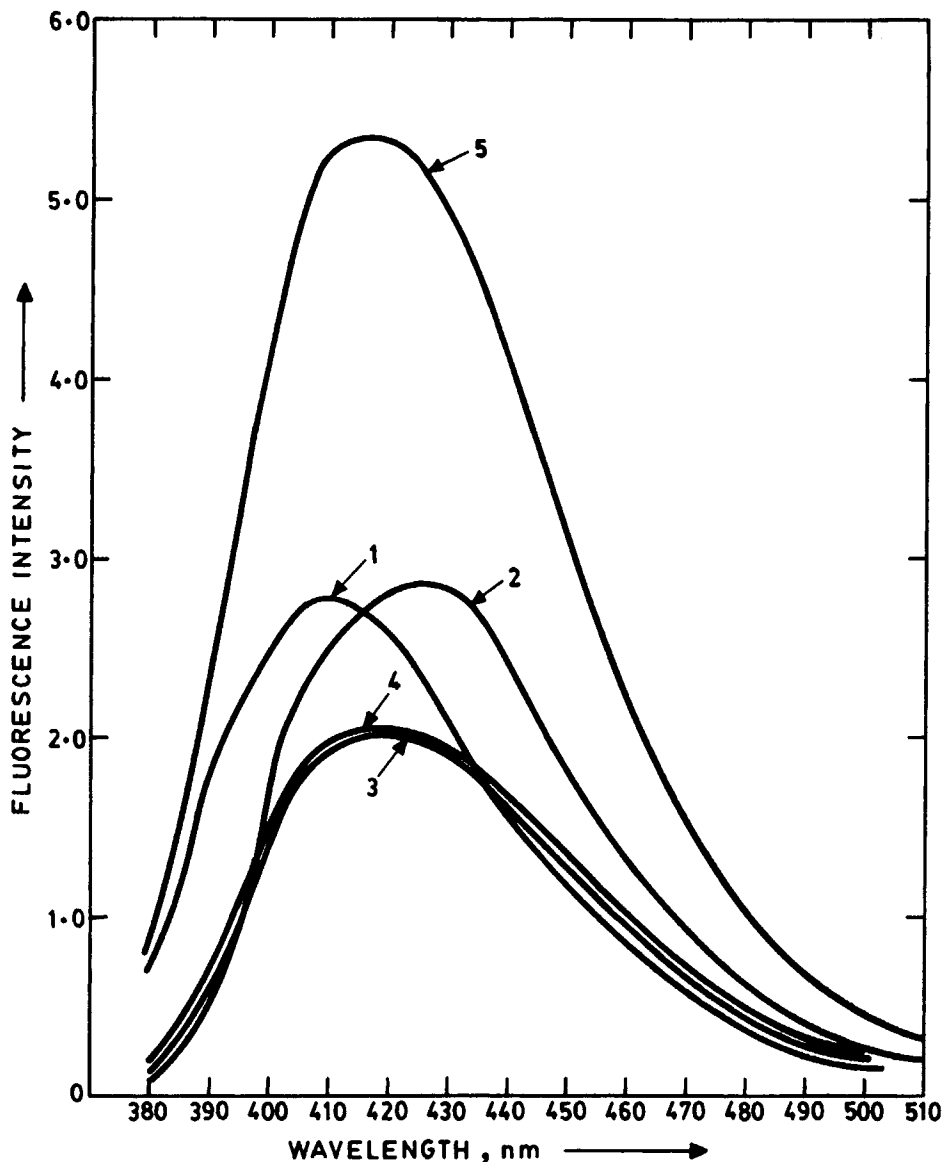


Fig. 5. Fluorescence spectra of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32 in the presence of PVP: (1) Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) + PVP (0.3 g/L), (2) Brightener 32 ( $0.25 \times 10^{-4}$  mol/L) + PVP (0.3 g/L), (3) Mixture of 1 and 2, (4) (Brightener 30 + Brightener 32) + PVP (0.3 g/L), (5) additive spectra of 1 and 2.

compound can interact with the dipole of the pyrrolidone ring because of the lactam bond. Such interaction can bring the molecules of the polymer and the compound closer to each other, and subsequently the short-range van der Waals and dispersion forces become operative, resulting in PVP-compound bonding.

The results obtained can be interpreted on the basis that PVP is effective in bringing about dissociation of the complex formed between the two com-



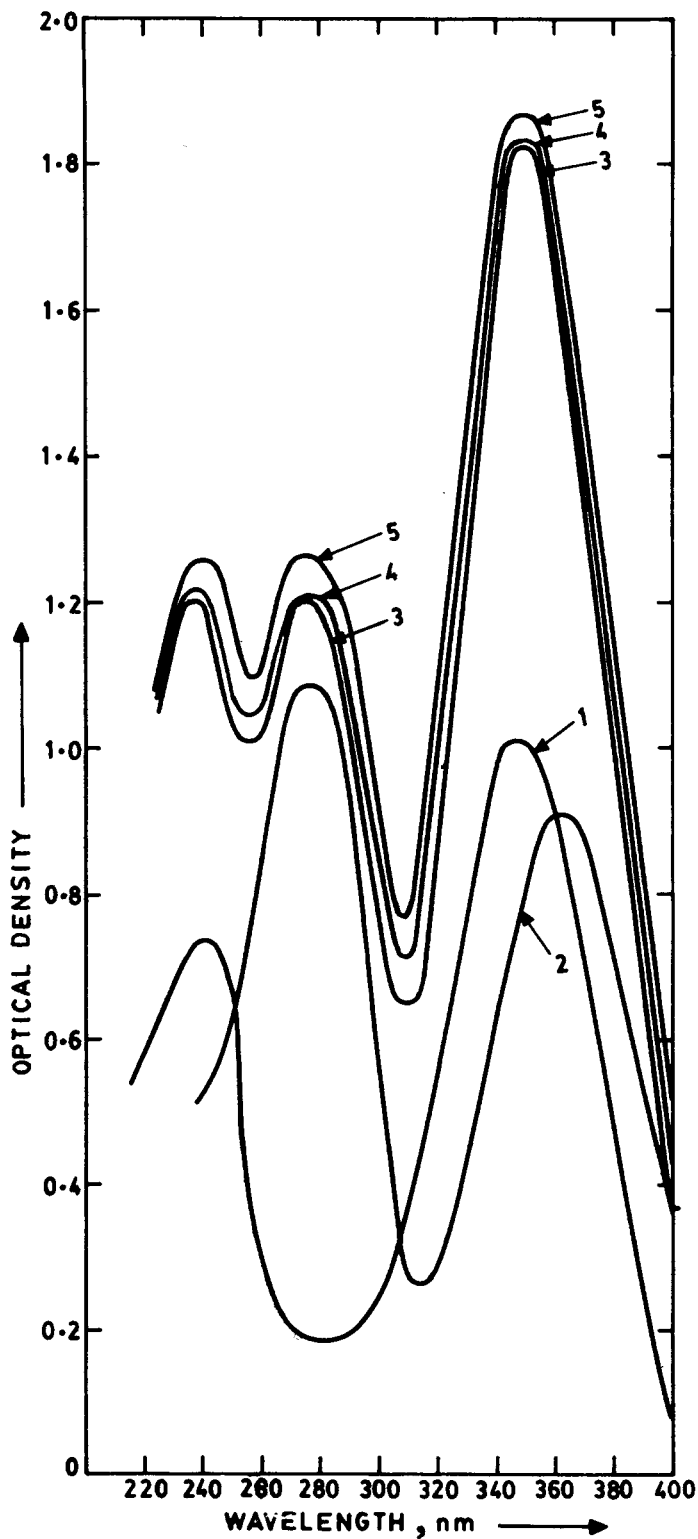


Fig. 6. Absorbance spectra of CI Fluorescent Brightener 30 and CI Fluorescent Brightener 32 in the presence of PVP: (1) Brightener 30 ( $0.25 \times 10^{-4}$  mol/L) + PVP (0.3 g/L), (2) Brightener 32 ( $0.25 \times 10^{-4}$  mol/L) + PVP (0.3 g/L), (3) Mixture of 1 and 2, (4) Brightener 30 + Brightener 32) + PVP (0.3 g/L), (5) additive spectra of 1 and 2.

pounds. The individual components so liberated then form complexes with PVP separately, and subsequently these complexes interact to form a different complex. Furthermore, it is also observed that the same type of complex is formed irrespective of whether the two compounds are mixed first and PVP added until the optimum concentration (beyond which there is no further change) or when each component is complexed first at optimum concentration of PVP and the two are then mixed subsequently. The critical concentration of PVP required for dissociation of the original complex between the two fluorescent compounds and formation of a new complex containing PVP, as observed from fluorescence and UV absorbance, does not depend on the molecular weight of PVP in the range of 10,000–750,000 examined.

### CONCLUSIONS

UV as well as fluorescence spectra of the mixture of CI Fluorescent Brighteners 30 and 32 are different from the additive spectra of the compounds when present individually, indicating interaction in the aqueous solution. The resulting complex shows fluorescence quenching.

Progressive addition of PVP to the mixture of the compounds results in an increase in the fluorescence intensity until, at a particular concentration, a maximum is reached beyond which there is no further change.

Progressive addition of PVP to the mixture of the compounds also results in an increase in absorbance at a longer wavelengths up to a specific concentration identical with that beyond which no further increase in fluorescence is observed. However, absorbance at shorter wavelengths does not change markedly up to this critical concentration of PVP, but at higher concentrations there is a rapid increase in the absorbance with a slight shift in  $\lambda_{\max}$ .

Results are explained on the basis of dissociation of the complex formed between the two fluorescent compounds due to presence of PVP, followed by interaction of each of the compounds liberated with PVP and subsequent formation of a different type of complex.

The same type of complex is formed irrespective of whether the two compounds are mixed first followed by addition of PVP up to a specific stage or when each component is complexed first with PVP and then the two are mixed subsequently.

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