

Studies in Interaction between Polyvinyl Pyrrolidone and Stilbene Fluorescent Compounds.

Part I: Interaction with Individual Compounds

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Synopsis

Interaction between polyvinyl pyrrolidone (PVP) and two stilbene-type fluorescent compounds has been examined from the results of emission, excitation, and ultraviolet absorbance measurements. Results obtained indicate preferential interaction of the *trans* form of the fluorescent compound with PVP resulting in complex formation and increase in fluorescence due to such complex formation. However, at higher concentrations of PVP in the aqueous phase the *cis* form also forms a complex which has no fluorescing characteristics. The calculated values of free energy change indicate weak bonding between both the fluorescent compounds and PVP. Fluorescent compound-binding capacity as well as the number of monomers of PVP combined remain more or less constant in the range of molecular weights of PVP studied.

INTRODUCTION

Interaction between polymeric compounds or surface-active agents with fluorescent colored or colorless compounds has been studied by several investigators¹⁻¹⁴ with a view to examine the effect of temperature, solvent medium, and structure of fluorescent compounds on such interactions. The nature of the interaction taking place has been arrived at from the results of changes in fluorescence and absorbance characteristics of the complex formed. However, little information is available in the literature regarding the behavior of the *cis* and *trans* form of the stilbene compounds with respect to interaction with polymers. The present work was therefore undertaken to examine the interaction between two stilbene types of fluorescent compounds and polyvinyl pyrrolidone (PVP) of different molecular weights by recording the changes in fluorescence as well as absorbance spectra of the complexes formed under different conditions.

EXPERIMENTAL

Polyvinyl pyrrolidone (PVP) having molecular weights of 10,000, 38,000, and 750,000 were obtained from GAF Corporation, U.S.A. while 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 α values of 1.4×10^{-4} and 0.70, respectively, as reported by Scholtan¹⁵ for converting intrinsic viscosity to viscosity average molecular weight.

C. I. Fluorescent Brightener 30 and Fluorescent Brightener 32, were se-

lected as stilbene-type fluorescent compounds having different constitutions. The compounds were first dissolved in DMF followed by precipitation with acetone to remove inorganic impurities. In the case of triazine type of Brightener 32, the triazine impurities were removed by extraction with toluene according to the method suggested by Weller.¹⁶ 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 cells, while emission and excitation spectra were recorded on an Aminco Bowman spectrofluorometer with 1 cm cells. Measurements were carried out at a compound concentration of 0.25×10^{-4} mol/L and different concentrations of PVP in the range of 0.01 to 10 g/L at 25°C and pH 7.0. At such concentrations, the fluorescent compounds in aqueous solution were found to be in a monomeric form as evident from spectrofluorometric measurements.

A mercury-tungsten lamp having little light emission below 380 nm (Light Fastness Tester of Microscal, U.K.) was used for irradiation of the aqueous solutions of the compound. Irradiation was carried out for 2 h in the presence of N₂ to prevent photo-oxidation of the fluorescent compounds. All solutions were kept in test tubes coated with black paint, to prevent transformation of the *trans* to the *cis* form.

RESULTS AND DISCUSSION

With both C. I. Fluorescent Brightener 30 and Fluorescent Brightener 32, progressive addition of PVP to the aqueous system under standard conditions of pH and temperature brings about an increase in the intensity of fluorescence. Results for C. I. Fluorescent Brightener 32 are shown in Figure 1. There is no shift of the λ_{\max} in the emission spectra. The critical concentration of PVP of molecular weight of 47,000 beyond which there is no change in the fluorescence intensity is different for the two brighteners studied, *viz.*, 0.3 g/L for C. I. Fluorescent Brightener 30 and 0.1 g/L for Fluorescent Brightener 32. However, in the case of excitation spectra, progressive addition of PVP results in a shift in λ_{\max} of 10 nm toward longer wavelengths and also an increase in the intensity at λ_{\max} till an optimum concentration of PVP is reached (Fig. 2). These optimum concentrations agree with those beyond which there is no further change in the emission spectra.

With respect to absorbance spectra, each of the fluorescent compounds shows two main absorbance bands, *viz.*, at 240 and 340 nm in case of C. I. Fluorescent Brightener 30 and 280 and 350 nm for Fluorescent Brightener 32. With progressive addition of PVP, absorbance at longer wavelengths increases and there is also a shift of λ_{\max} up to a critical stage, beyond which there is little change on further addition of PVP. An isobestic point is also observed for absorbance at longer wavelengths (Figs. 3 and 4). On the other hand, there is limited change in the absorbance at shorter wavelengths at lower amounts of PVP added, but beyond a certain concentration, there is a rapid increase in the absorbance in this region with a slight shift in the λ_{\max} to shorter wavelengths. PVP itself does not absorb in the region of ultraviolet light used in the study. In both compounds, optimum con-

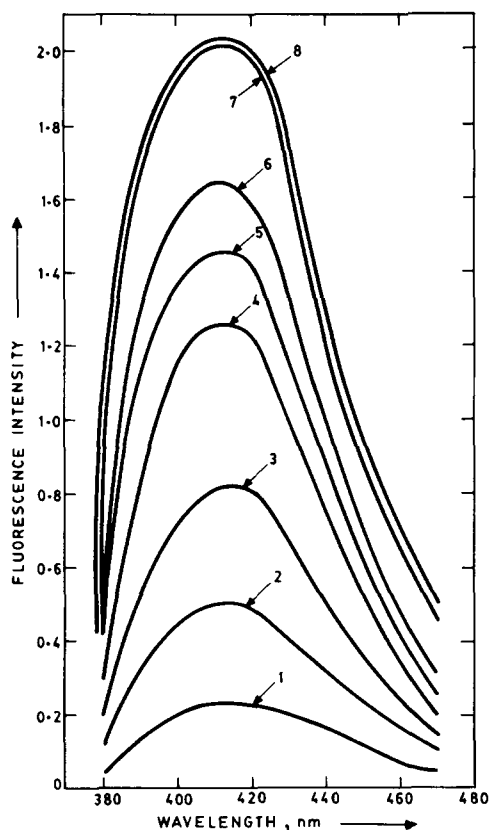


Fig. 1. Emission spectra of PVP-C. I. Fluorescent Brightener 30 Complex. 1 Brightener along (0.25×10^{-4} mol/L), 2 Brightener + PVP (0.01 g/L), 3 Brightener + PVP (0.03 g/L), 4 Brightener + PVP (0.05 g/L), 5 Brightener + PVP (0.07 g/L), 6 Brightener + PVP (0.1 g/L), 7 Brightener + PVP (0.3 g/L), 8 Brightener + PVP (10.0 g/L).

centrations of PVP beyond which there is no increase in the fluorescence intensity corresponds fairly well with the concentrations beyond which changes in the absorbance at longer wavelengths are negligible.

These results can be explained on the basis that interaction takes place between the fluorescent compound and PVP in the aqueous solution. In the two stilbene-type compounds, both the *cis* and the *trans* forms coexist with each other in the aqueous solution. It is known that only the *trans* form has fluorescing characteristics.⁹ Thus, the increase in fluorescence observed on addition of PVP is mainly due to the complexing of PVP with the *trans* form in the aqueous phase, and the resulting complex has greater fluorescing ability compared with that of the uncomplexed *trans* form of the compound. This is supported by the fact that absorbance at longer wavelengths, which is characteristic of the *trans* form, *viz.*, 340 nm for C. I. Fluorescent Brightener 30 and 350 nm for Fluorescent Brightener 32, changes simultaneously until the complex formation is more or less complete (Figs. 3 and 4). It is observed that the concentration of PVP beyond which there is practically no change in either fluorescence or absorbance at longer wavelengths corresponds with the concentration where there is little change in

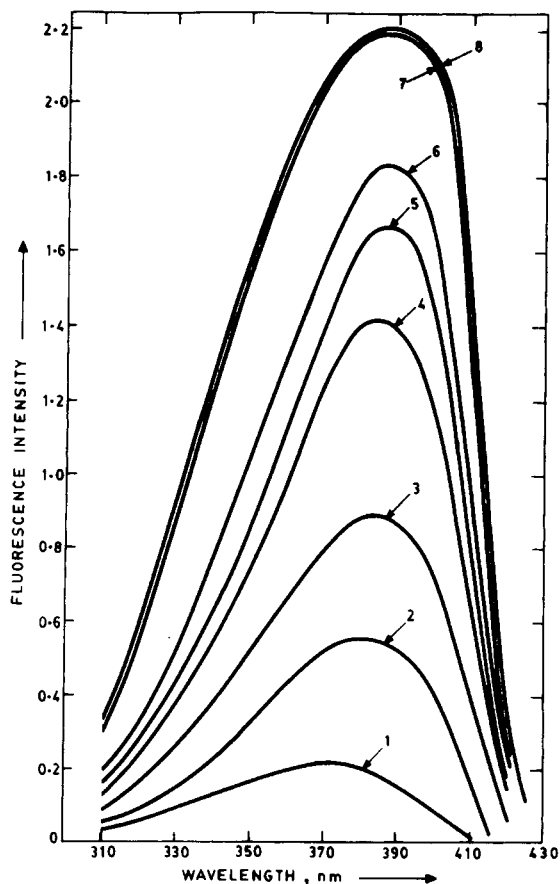


Fig. 2. Excitation spectra of PVP-C. I. Fluorescent Brightener 30 Complex. 1 Brightener alone (0.25×10^{-4} mol/L), 2 Brightener + PVP (0.01 g/L), 3 Brightener + PVP (0.03 g/L), 4 Brightener + PVP (0.05 g/L), 5 Brightener + PVP (0.07 g/L), 6 Brightener + PVP (0.1 g/L), 7 Brightener + PVP (0.3 g/L), 8 Brightener + PVP (10.0 g/L).

the absorbance at shorter wavelengths, which is due to the *cis* form of the compound in the aqueous solution. However, when the concentration of PVP in the system is increased beyond a specific stage where more or less all of the *trans* form has complexed with the polymer, there is a rapid increase in the absorbance at shorter wavelengths. This proves that after the preferential complex formation between PVP and the *trans* form of the compound, another type of nonfluorescing complex is also formed between PVP and the *cis* form of the brightener.

Further evidence of complex formation between PVP and both the *cis* and the *trans* forms of the stilbene compounds is available from the results of studies in the aqueous solutions of the compounds after irradiation to a source emitting light of wavelengths greater than 380 nm followed by addition of PVP at specific concentrations. It is observed that on irradiation of aqueous solutions of the compounds, intensity of absorbance at longer wavelengths is suppressed, while that at shorter wavelengths is increased,

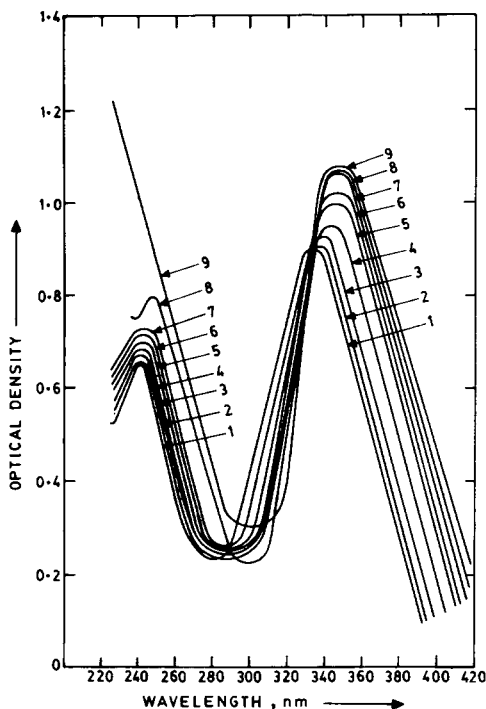


Fig. 3. Absorbance spectra of PVP-C. I. Fluorescent Brightener 30 Complex. 1 Brightener alone (0.25×10^{-4} mol/L), 2 Brightener + PVP (0.01 g/L), 3 Brightener + PVP (0.03 g/L), 4 Brightener + PVP (0.05 g/L), 5 Brightener + PVP (0.07 g/L), 6 Brightener + PVP (0.1 g/L), 7 Brightener + PVP (0.3 g/L), 8 Brightener + PVP (5.0 g/L), 9 Brightener + PVP (10.0 g/L).

indicating conversion of the *trans* form to the *cis* form during irradiation (Fig. 5). Although the source of light used emitted limited radiations below 380 nm, the quantity was sufficient to convert appreciable amounts of the *trans* form to the *cis* state, since there is significant absorption by the *trans* isomer in this region. Under the conditions of irradiation used, there is hardly any absorption by the *cis* isomer and, therefore, the reverse change from *cis* to *trans* form is discouraged. Similar results have been obtained by Weller¹⁶ for four different stilbene-type compounds. After irradiation, when PVP is added to the irradiated solutions at a lower concentration of PVP, there is only a limited change in the absorbance by the *trans* form, because after irradiation most of the original *trans* form has been converted to the *cis* form. There is practically no change for the absorbance corresponding to the *cis* form. However, when the concentration of PVP is increased further, considerable increase in the absorbance of the *cis* band takes place simultaneously with some increase in the intensity for absorbance of the *trans* form. This clearly indicates that complex formation between PVP and both the *trans* and the *cis* forms does take place. However, such complex formation has been found to be preferential with the *trans* form, and, only after the *trans* form has complexed with PVP does interaction with the *cis* form of the compound take place.

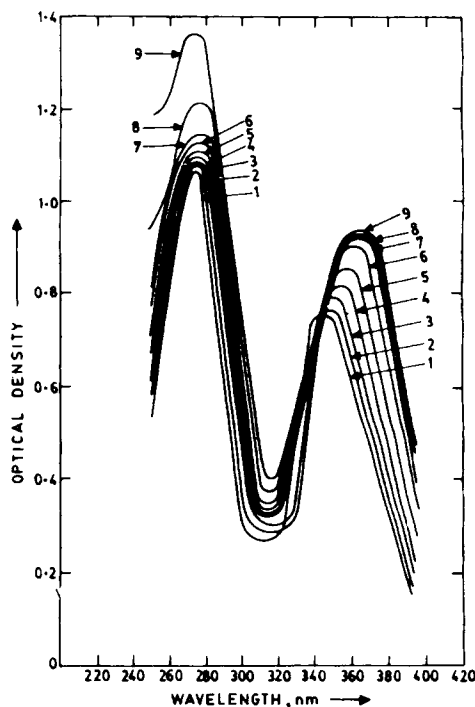


Fig. 4. Absorbance spectra of PVP-C. I. Fluorescent Brightener 32 Complex. 1 Brightener alone (0.25×10^{-4} mol/L), 2 Brightener + PVP (0.01 g/L), 3 Brightener + PVP (0.03 g/L), 4 Brightener + PVP (0.05 g/L), 5 Brightener + PVP (0.07 g/L), 6 Brightener + PVP (0.1 g/L), 7 Brightener + PVP (0.3 g/L), 8 Brightener + PVP (5.0 g/L), 9 Brightener + PVP (10.0 g/L).

When comparison is made of the absorbance characteristics of the irradiated and unirradiated solution of the compounds on progressive addition of PVP, certain differences are observed. In unirradiated solution, in the initial stages of PVP addition, there is considerable change in the absorbance at longer wavelengths, but beyond a critical concentration of PVP there is hardly any change in the absorbance by the *trans* form. However, under these conditions there is a substantial increase in the absorbance by the *cis* form. On the other hand, with the irradiated solution, changes at longer wavelengths, corresponding to complex formation by the *trans* form is progressive although limited, and even at higher concentrations of PVP there is some increase in the absorbance at this wavelength. This is because a substantial quantity of the *cis* form coexists with a small quantity of the *trans* form in the irradiated solution. As more and more of the *trans* form complexes with PVP, there is a shift in the relative proportions of *cis* and *trans* forms. As a result, more of the *trans* form which is now available in the aqueous phase gets complexed with PVP (Fig. 5).

Fluorescence spectra for both compounds examined in the presence of PVP indicate the existence of equilibrium between the free *cis* and *trans* forms of the compound in the aqueous solution and the *trans* form complexed with PVP, depending on the amount of PVP present in the system.

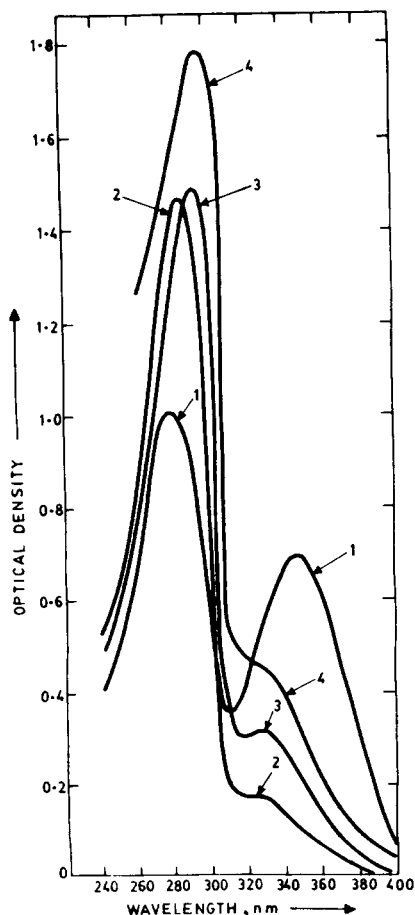


Fig. 5. Absorbance spectra of PVP-C. I. Fluorescent Brightener 32 Complex. 1 Brightener (0.25×10^{-4} mol/L) before irradiation, 2 Brightener after irradiation, 3 Brightener after irradiation + PVP (0.1 g/L), 4 Brightener after irradiation + PVP (10.0 g/L).

From this it is possible to calculate the relative amounts of free and bound fluorescent compound from the measured fluorescence intensity, according to the method suggested by Killman.¹² The characteristic plots correlating free compound in solution ($C\sigma$) and the bound one ($C\phi$) at pH 7 for both compounds are shown in Figure 6. To determine the maximum fluorescent compound-binding capacity of the *trans* form for PVP, reciprocal plots of the bound and the free compounds in the system have been obtained (Fig. 7). These plots indicate a Langmuir-type interaction between these compounds and PVP. From the intercepts on the axis corresponding to reciprocal of bound fluorescent compound, the total binding capacity of each compound for PVP of specific molecular weight under standard conditions of pH and temperature has been obtained (Table I). The maximum binding capacity for PVP as well as the number of monomer units of PVP per mole of the compound remain more or less the same, irrespective of the molecular weight of PVP in the range of 10,000–750,000. These results show that,

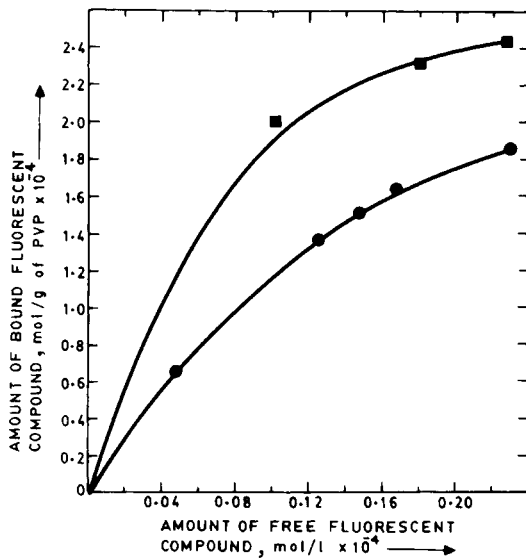


Fig. 6. Interaction isotherms for Fluorescent Brightener-PVP complexes. (●) C. I. Fluorescent Brightener 30, (■) C. I. Fluorescent Brightener 32.

although the molecular weight of PVP is increased by 75 times, the configuration of the polymer molecule in the aqueous solution changes in such a way that no additional sites in the PVP molecule are available for interaction with the compounds.

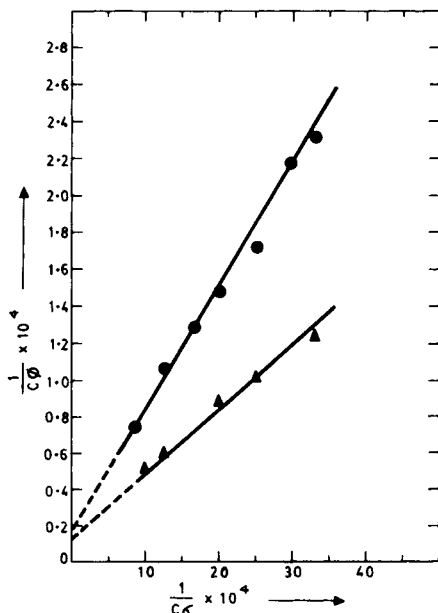


Fig. 7. Klotz plots for interaction of Fluorescent Brighteners with PVP. (●) C. I. Fluorescent Brightener 30, (▲) C. I. Fluorescent Brightener 32.

TABLE I
 Maximum Fluorescent Compound Binding Capacity and Number of Monomers of PVP for Interaction between Stilbene Fluorescent Compounds and PVP of Different Molecular Weight at 25°C and pH 7.0

Fluorescent compound	Molecular weight of PVP							
	10,000		38,000		47,000		750,000	
	Maximum binding capacity, mol/kg PVP	Number of monomers of PVP/mol of compound	Maximum binding capacity, mol/kg PVP	Number of monomers of PVP/mol of compound	Maximum binding capacity, mol/kg PVP	Number of monomers of PVP/mol of compound	Maximum binding capacity, mol/kg PVP	Number of monomers of PVP/mol of compound
C.I. Fluorescent Brightener 30	0.833	10.8	0.833	10.8	0.714	12.6	0.714	12.6
C.I. Fluorescent Brightener 32	0.833	10.8	0.833	10.8	0.833	10.8	0.833	10.8

Values of free energy change (ΔF) have been obtained on the basis of Klotz equation

$$\frac{1}{C\phi} = \frac{1}{KC\sigma C_s} + \frac{1}{C_s}$$

where K is the binding constant and C_s the saturation value. Values of K are obtained from the slope of the linear plots correlating $\frac{1}{C\phi}$ with $\frac{1}{C\sigma}$ and values of C_s from the intercepts on the $\frac{1}{C\sigma}$ axis. ΔF has been obtained from the relation

$$\Delta F = \Delta - RT \ln K$$

where R and T are gas constant and absolute temperature, respectively. Values for the complex formation between the *trans* form of the compounds and PVP are fairly low, *viz.*, -7.5 to -10.9 kJ/mole, suggesting that these complexes have low energy of association. Furthermore, there is practically no change in this parameter for the complex formation with PVP of different molecular weights.

CONCLUSIONS

Studies in interaction of PVP of different molecular weights with two stilbene-type fluorescent compounds have been carried out employing fluorometric and ultraviolet spectrophotometric measurements of the aqueous solutions. Results obtained:

1. At lower concentrations of PVP in the system there is a marked increase in the emission, excitation, and ultraviolet absorbance at longer wavelengths.

2. Critical concentrations of PVP beyond which there is no change in fluorescence and absorbance at longer wavelengths are nearly the same, but differ depending on the chemical constitution of the fluorescent compound.

3. At a higher concentration of PVP in the system, there is no further change in the fluorescence or ultraviolet absorbance at longer wavelengths, but a marked increase in the absorbance at shorter lengths occurs.

4. Results are interpreted on the basis of preferential complex formation between the *trans* form of the compound at a lower concentration of PVP in the system but at a higher concentrations the *cis* form also interacts with PVP.

5. The mechanism of interaction can be best represented by weak bonding forces operating between the fluorescent compound and PVP.

6. The extent of interaction does not appear to depend on the molecular weight of PVP in the range of molecular weights studied.

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