

# Studies in Interaction between Poly(vinyl Pyrrolidone) and Azo Dyes

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## Synopsis

Interaction between poly(vinyl pyrrolidone) (PVP) and monoazo dyes containing different numbers of ionic groups situated at different locations in the dye molecule has been examined from the results of spectrophotometric, conductometric, and viscosity measurements. Results indicate the maximum dye binding capacity as well as number of monomer units of PVP combined with the molecule of dye depends on the number of ionic groups present in the dye molecule but not on the location of these groups. The calculated values of free energy change indicate weak bonding between the dyes examined and PVP at different pH's in the range of 4–10.7. Dye binding capacity as well as number of monomers of PVP combined also depend on the molecular weight of PVP. Changes in the configuration of the polymer molecule of PVP take place as a result of dye-polymer interaction.

## INTRODUCTION

Poly(vinyl pyrrolidone) (PVP) is a versatile polymer which is widely used for a variety of purposes including cosmetics and toiletries, textiles and dyes, pharmaceuticals, adhesives, etc. PVP has the unusual property of forming complexes with different substances. Several studies have been carried out with respect to interaction of PVP with inorganic and organic compounds, with special reference to total number of binding sites available for the interaction, free energy and heat of interaction, and changes in the shape of polymer molecule resulting from adsorption of dyes.<sup>1-6</sup> However, only limited information is available with respect to the effect of substituent ionic groups in the dye molecule and the location of these groups on the interaction with PVP of different molecular weights. It was, therefore, thought desirable to study the interaction between PVP of specific molecular weight and monoazo dyes having the same chromophore but containing different number of ionic groups situated at different locations in the dye molecule.

## EXPERIMENTAL

PVP having molecular weights of 10,000, 38,000, and 750,000 were obtained from GAF Corp. while PVP of molecular weight 47,000 was obtained from Calico Chemicals, 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>7</sup> for converting intrinsic viscosity to viscosity-average molecular weight.

C.I. Acid Red 11, Acid Red 44, Acid Red 18, and Acid Red 9 were selected as the monoazo dyes wherein the first three dyes had the same chromophore

but one, two, and three anionic sulfonic acid groups present in the dye molecule, respectively, while in case of Acid Red 9, although it contained three sulfonic acid groups as that in Acid Red 18, the location of these groups was different. Dyes were purified by first dissolving in dimethyl formamide followed by precipitation by acetone, according to the method recommended by Hall and Perkins.<sup>8</sup> Purity of the dyes was checked chromatographically and also colorimetrically.

Absorbance values of solutions of the dyes containing PVP were obtained on a Bausch and Lomb spectrophotometer with 1 cm cell. Measurements were carried out at constant concentration of the dye ( $0.5 \times 10^{-5}$  mol/L in case of C.I. Acid Red 11 and  $0.25 \times 10^{-4}$  mol/L for C.I. Acid Red 18, 44, and 9) and different concentrations of PVP (0.05–100 g/L) at 25°C and at pH 4, 7, and 10.5. At these concentrations of the dye, the specific dye was present in the aqueous solution in monomeric form as evident from spectrophotometric measurements. Amounts of free dye in the aqueous phase in equilibrium with that of dye bound to PVP was calculated from absorbance values according to the spectrophotometric method used by Stevenson et al.<sup>9</sup> for the study of interaction between monoazo dyes and different surface-active agents.

Conductivity measurements were carried out on CLO1/01A conductivity bridge with cell constant of 0.804 at 27°C. For viscosity measurements, Ostwald viscometer no.1 was used and the temperature was maintained at  $27 \pm 0.05^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The spectra for the four dyes examined at constant concentration of the dye in aqueous solution with varying concentrations of PVP at pH 7 show a characteristic feature in that there is an intersection of the spectral curves over a narrow range of wavelength and absorbance. The spectral curves for C.I. Acid Red 44 are shown in Figure 1. Similar spectral behavior was found for the other dyes also, both at pH 7 and also at pH 4 and 10.5.

Absorbance spectra for the four dyes examined in the presence of PVP indicate the existence of free dye as well as the bound dye in equilibrium, depending on the concentration of PVP present in the system. On the basis of this, it is possible to calculate the relative amounts of free and bound dye from the measured absorbance.<sup>9</sup> The characteristic plots correlating free dye in solution ( $C\sigma$ ) and bound dye ( $C\phi$ ) at pH 7 in case of C.I. Acid Red 11 and Acid Red 44 are shown in Figure 2. In order to determine the maximum dye-binding capacity for PVP, reciprocal plots of the bound dye and the free dye in the system have been obtained (Fig. 3). These plots indicate a Langmuir type of interaction between these dyes and PVP. From the intercepts on the axis corresponding to reciprocal of bound dye, the total binding capacity of each dye for PVP under standard conditions of pH and temperature have been obtained. Values for free energy change ( $\Delta F$ ) were calculated for each dye at different pH. These values along with the values for maximum dye-binding capacity and number of monomer units of PVP combined with 1 mol of dye are given in Table I.

Additional evidence of interaction between the dyes studied and PVP has been obtained from conductivity measurements. When plots correlating

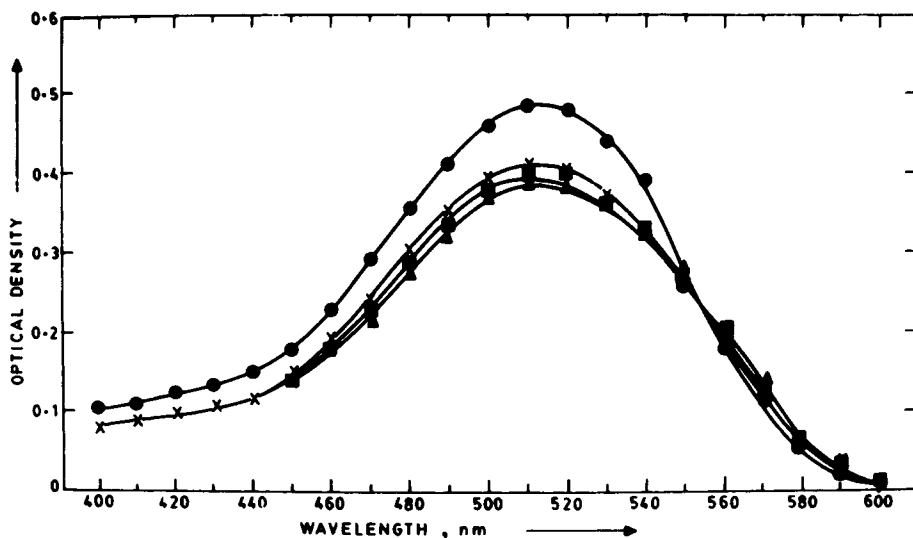


Fig. 1. Absorbance spectra of the PVP-C.I. Acid Red 44 complex: (●) dye alone ( $0.25 \times 10^{-4}$  mol/L); (X) dye + PVP (0.5 g/L); (■) dye + PVP (1.0 g/L); (▲) dye + PVP (2.0 g/L).

specific conductivity and concentration of PVP were obtained, it was observed that, at a specific concentration of PVP for each dye, there was a marked change in the direction of the two linear curves and the critical concentration at which such changes occurred were different for the mono-, di-, and trisulfonated monoazo dyes (Fig. 4). These values of PVP correspond to the maximum amount of PVP required for the interaction with constant concentration of each dye in the aqueous phase, and they agree fairly well with the corresponding values determined from spectrophotometric measurements made in the present study (Table II).

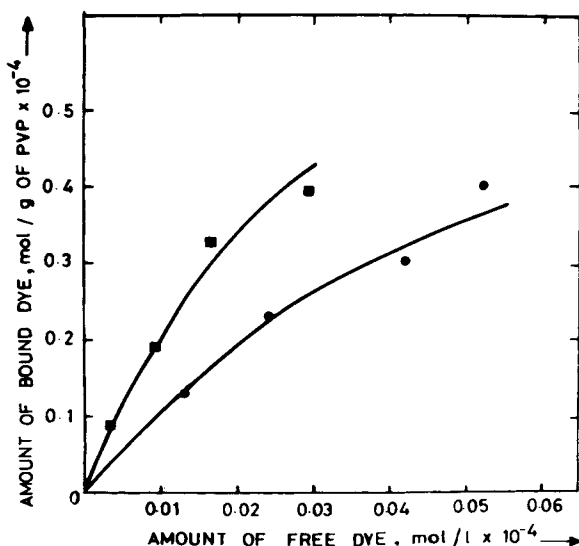


Fig. 2. Interaction isotherms for monoazo dyes-PVP complex: (■) C.I. Acid Red 11; (●) C.I. Acid Red 44.

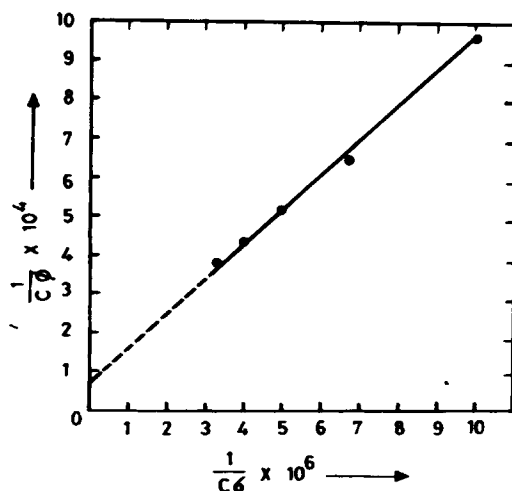


Fig. 3. Klotz plot for interaction of C.I. Acid Red 44 with PVP.

$\Delta F$  values for all the dyes examined for interaction with PVP of different molecular weights are quite low and vary between  $-1.5$  and  $-4.0$  kcal/mol, indicating weak bonding between dyes examined and PVP at  $25^\circ\text{C}$  and at different pH. This is substantiated by the fact that when absorption spectra of the dye-PVP complex was determined at  $50^\circ\text{C}$ , it appeared that the complex was destroyed at this temperature (Fig. 5). These values for the four dyes are lower than those reported by Frank et al.<sup>2</sup>, viz.,  $-6.7$  kcal/mol for interaction between a monoazo dye C.I. Acid Orange 7 and  $-8.5$  kcal/mol for a disazo dye C.I. Direct Red 2 with PVP, employing dialysis technique of measurement. The maximum binding capacity of each dye for PVP is different and decreases in the order mono-, di-, and trisulfonated dye. There is no difference in the maximum binding capacity of the two trisulfonated dyes studied, indicating that the location of the sulfonic acid group in dye molecule has little effect on this parameter.

From the values of  $\Delta F$ , it appears that primary van der Waal's forces between the aromatic system of the dye anion and the paraffin chain of the PVP molecule are likely to be responsible for the interaction. Although Scholtan<sup>8</sup> has suggested that H bonds may to some extent contribute to the forces of interaction between PVP and monoazo dyes, it is unlikely that such a mechanism can be operative in aqueous solutions. The monoazo dyes studied can assume a flat configuration, and maximum interaction is then

TABLE I  
Maximum Dye Binding Capacity, Free Energy Change, and Number of Monomers of PVP for Interaction between Monoazo Dyes and PVP at  $25^\circ\text{C}$  and pH 7.0

Dye	Maximum dye binding capacity (mol/kg PVP)	$\Delta F$ (k cal/mol)	Number of monomers of PVP/mol of dye
C.I. Acid Red 11	0.3125	$-2.6$	28
C.I. Acid Red 44	0.0398	$-1.6$	226
C.I. Acid Red 18	0.0331	$-1.8$	272
C.I. Acid Red 9	0.0331	$-2.5$	272

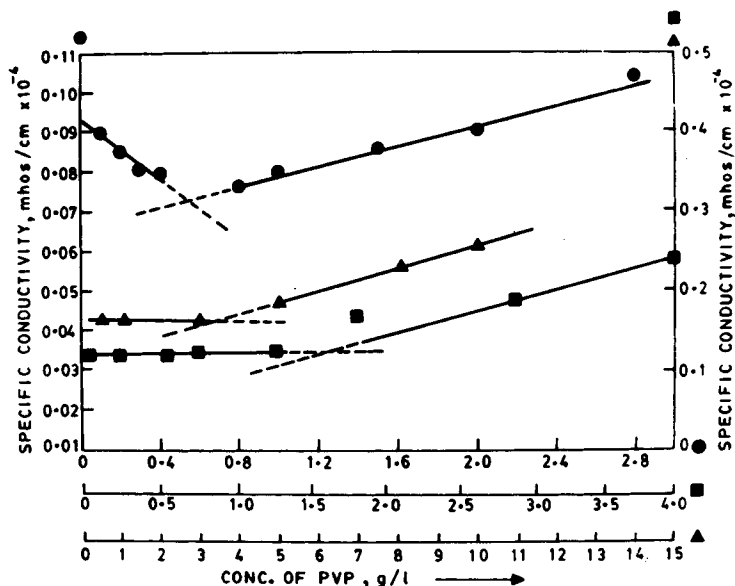


Fig. 4. Plots of specific conductivity of monoazo dyes at different PVP concentrations: (●) C.I. Acid Red 11; (■) C.I. Acid Red 44; (▲) C.I. Acid Red 18.

possible through an alignment of the dye molecules with the paraffin chains. As bulky substituents are present in the polyvinyl chain of PVP, much rotation round the C—C bonds does not seem possible and PVP molecule can then assume a fairly stiff configuration. The PVP-dye complex appears to be similar to the complexes formed between different proteins and charged organic compounds, except that, with the later systems, binding is mainly due to the electrostatic attraction between opposite charges in addition to the intermolecular forces of other type. Under conditions of pH studied, the PVP molecule does not appear to acquire any charge. This has been substantiated from the results of electrophoresis measurements carried out in the present study. In view of this, the binding can be mainly due to intermolecular forces. The lactam bond in the pyrrolidone ring is likely to induce ion-dipole interaction with the dye which, in turn, will assist in bringing the dye molecule in close contact with the PVP, and subsequently the short range dispersion forces will then become operative leading to the stabilization of the complex.

From the experimentally determined molecular weight of PVP (47,000) and the maximum dye binding capacity for each dye, the number of mono-

TABLE II  
Maximum Concentration of PVP Obtained from Conductometric and Spectrophotometric Measurements

Dye	Maximum concn of PVP (g/L)	
	Conductometry	Spectrophotometry
C.I. Acid Red 11	0.5	0.5
C.I. Acid Red 44	1.7	2.0
C.I. Acid Red 18	3.4	3.0

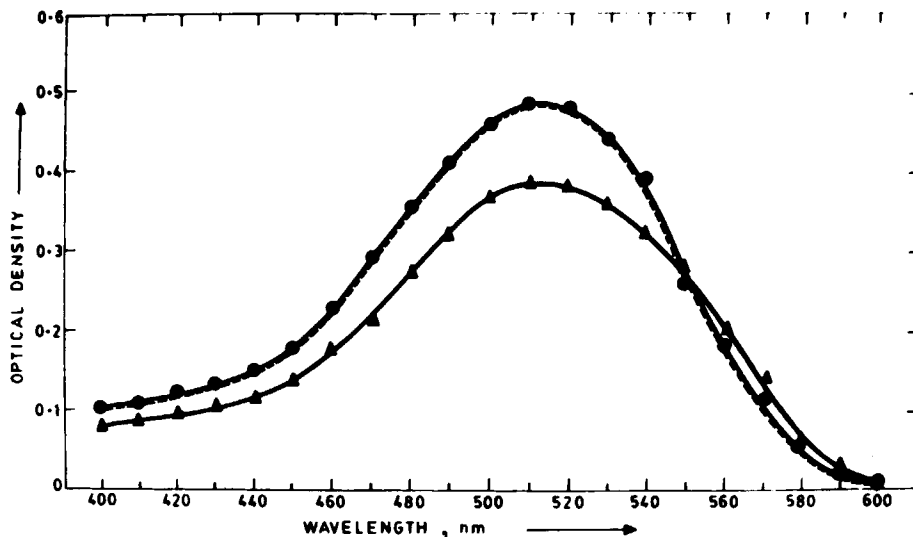


Fig. 5. Effect of temperature on complex between C.I. Acid Red 44 and PVP: (●) dye alone ( $0.25 \times 10^{-4}$  mol/L); (▲) dye + PVP (2.0 g/L) at 25°C; (- - -) dye + PVP (2.0 g/L) at 50°C.

mer units of PVP per molecule of mono-, di-, and trisulfonated dyes, viz., 29, 226, and 272, respectively, have been calculated. The value of 29 monomers in case of monosulfonated dye agrees with the value of 29 monomers calculated from the results of Sivaraja Iyer and Singh<sup>10</sup> for the monoazo dye C.I. Acid Orange 7 with PVP employing polarographic technique. However, this value for the monomer units is higher than the value obtained by Frank et al.<sup>2</sup>, viz., 5.5 monomers in the presence of KCl and 7.0 in the absence of KCl for C.I. Acid Orange 7-PVP complex, obtained from the results of dialysis experiments. If maximum packing is assumed between the dyes and PVP polymer chain, about three monomer units of PVP should correspond to each dye molecule because the length of the monomer unit repeat for PVP is 4.5Å and the length of the dye molecule is about 13Å.

The present results also indicate that the number of monomer units corresponding to the binding site for the dye molecule increases as the number of ionic sulfonic acid groups in the dye molecule increases. This goes to show that the packing of the dye molecule on the PVP polymer chain backbone is affected adversely due to the bulky sulfonic acid groups present in the dye molecule. However, the location of the sulfonic acid group has little effect on the number of monomer units for binding site per dye molecule, as indicated by the fact that in case of C.I. Acid Red 18 and Acid Red 9, the number of monomers is the same, although the three sulfonic acid groups in the molecules of these dyes are situated at different locations.

In order to determine the changes in the configuration of the molecule of PVP during interaction with monoazo dyes studied, viscosity measurements were carried out. In the absence of electrolyte, the value of reduced viscosity first increases and then decreases as the concentration of PVP in the solution increases (Fig. 6). The reduced viscosity passes through a maximum corresponding to a specific concentration of PVP depending on the number of sulfonic acid groups present in the molecule of the dye. The

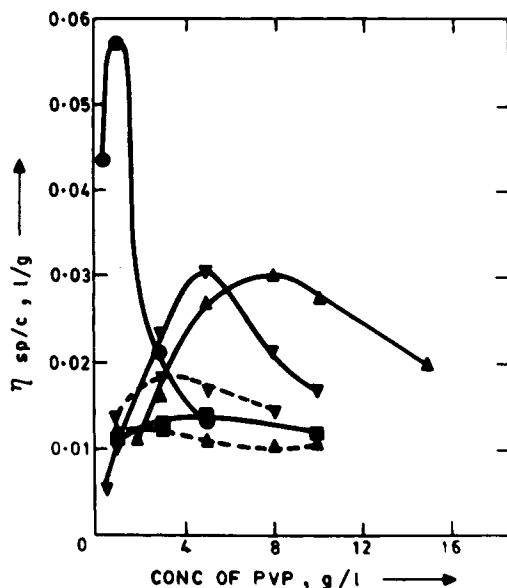


Fig. 6. Plots of reduced viscosity of complexing between monoazo dyes and PVP: (●) C.I. Acid Red 11 ( $0.5 \times 10^{-5}$  mol/L) (▼) C.I. Acid Red 44 ( $0.25 \times 10^{-4}$ ); (▲) C.I. Acid Red 18 ( $0.25 \times 10^{-4}$  mol/L); (-▼-) C.I. Acid Red 44 with  $0.4M$  KCl; (-▲-) C.I. Acid Red 18 with  $0.4M$  KCl; (■) PVP alone.

value for this maximum concentration of PVP increases as the number of sulfonic acid groups in the dye molecule increases. The increase in the reduced viscosity during the initial stages with an increase in the concentration of PVP can be attributed to increase in complex formation between the dye and PVP. Thus, at a definite concentration of PVP, a maximum in the reduced viscosity is observed. The reduction in the reduced viscosity with increasing concentration of PVP beyond the maximum is characteristic of the behavior of polyelectrolytes, in which case the electrostatic repulsion of identical charges is so altered that folding of the molecule of the polymer molecule may take place. However, when electrolyte is added to the system, the electroviscous behavior is more or less completely suppressed, and there is an overall reduction in the reduced viscosity at all PVP concentrations studied. This is evident from the fact that the viscosity curve in presence of  $0.4M$  KCl for C.I. Acid Red 18 is comparable with the reference curve of PVP.

In order to obtain maximum dye binding capacity and number of monomer units of PVP per dye molecule for interaction between different dyes and PVP of molecular weights 10,000, 38,000, and 750,000, spectrophotometric measurements were carried out as mentioned before and the values compared with those for PVP of molecular weight of 47,000 (Tables I and III).

It may be noted that the behavior as was observed with PVP of molecular weight 47,000 is also reflected in case of PVP of different molecular weights. Maximum dye binding capacity decreases and the number of monomer units of PVP per mole of dye increases as the number of sulfonic acid groups in the dye molecule increase, although the values are different from PVP of

TABLE III  
 Maximum Dye Binding Capacity and Number of Monomers of PVP for Interaction between Monoazo Dyes and PVP of Different  
 Molecular Weight at 25°C and pH 7.0

Dye	Molecular weight of PVP					
	10,000		38,000		750,000	
	Maximum dye binding capacity (mol/kg PVP)	Numbers of monomers of PVP/mol of dye	Maximum dye binding capacity (mol/kg PVP)	Number of monomers of PVP/mol of dye	Maximum dye binding capacity (mol/kg PVP)	Number of monomers of PVP/mol of dye
C.I. Acid Red 11	0.0833	109	0.1389	65	0.3125	29
C.I. Acid Red 44	0.0199	452	0.0398	226	0.0398	226
C.I. Acid Red 18	0.0075	1196	0.0331	272	0.0331	272



different molecular weights. Furthermore, with PVP of low molecular weight (10,000), the decrease in maximum dye binding capacity from mono- to di- to trisulfonated dye is quite marked, but, with higher molecular weight PVP, the difference between di- and trisulfonated dyes is not appreciable. Similarly, increases in the maximum dye binding capacity for the monosulfonated dye is appreciable when the molecular weight of PVP is increased from 10,000 to 47,000 while, in the case of di- and trisulfonated dyes, beyond a molecular weight of 38,000 there is no further increase. It is likely that, beyond a critical chain length of PVP, the configuration of polymer molecule changes in such a way that no additional sites are available for interaction with the dye.

### CONCLUSION

Studies in the interaction of PVP of different molecular weight with monoazo dyes has been examined employing spectrophotometric, conductometric, and viscosity measurements of the aqueous solutions at different temperatures and pH. Results obtained can be summarized as follows:

1. Maximum dye binding capacity and number of monomer units of PVP combined with a mole of dye are greatly dependent on the number of ionic sulfonic acid groups present in the dye molecule but not on their location.

2. PVP in the range of pH 4–10.7 does not acquire electrical charge and the mechanism of interaction can be best represented by weak bonding of the primary van der Waal's forces operating between the dye and PVP.

3. Extent of interaction depends on the molecular weight of PVP. With low molecular weight PVP, decrease in maximum dye binding capacity from mono- to di- to trisulfonated dye is quite marked, but, with higher molecular weight PVP, the difference is not appreciable.

4. Although maximum dye binding capacity for monosulfonated dye is appreciable when the molecular weight of PVP is increased from 10,000 to 47,000, with di- and trisulfonated dyes, beyond molecular weight of 38,000 there is no further increase in this parameter.

5. Configuration of PVP molecule in the dye–PVP complex in aqueous solution is dependent on the concentration of PVP as revealed by the fact that the reduced viscosity of the solution in absence of an electrolyte first increases, reaches a maximum and then decreases as the concentration of PVP is progressively increased.

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### References

1. S. M. Barkin, H. P. Frank, and F. R. Eirich, *Ricerca Sci.* **25**, *Suppl., Simp. Int. Chim. Macromol., Milan-Turin*, 844 (1955).
2. H. P. Frank, S. Barkin, and F. R. Eirich, *J. Phys. Chem.*, **61**, 1375 (1957).
3. W. Scholtan, *Makromol. Chem.*, **11**, 131 (1953).
4. P. Molyneux and H. P. Frank, *J. Am. Chem. Soc.*, **83**, 3169 (1961).
5. W. Luck, *J. Soc. Dyers Colour.*, **74**, 221 (1958).
6. E. C. Hansen, C. A. Bergman, and D. B. Witwer, *Am. Dyestuff Rep.*, **43**, 72 (1954).
7. W. Scholtan, *Makromol. Chem.*, **7**, 209 (1951).

8. D. M. Hall and W. S. Perkins, *Text. Res. J.*, **41**, 923 (1971).
9. D. M. Stevenson, D. G. Duff, and D. J. Kirkwood, *J. Soc. Dyers Colour.*, **97**, 13 (1981).
10. S. R. Sivaraja Iyer and G. S. Singh, in *Physicochemical Aspects of Interaction of Dyes in Solution and in Fibre System*, University of Bombay, 1969, p. 32.

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