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The aggregation of triphenodioxazine reactive dyes in aqueous solution and on cellulosic and nylon substrates

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Abstract

Monomer–dimer equilibriums of triphenodioxazine (TPDO) reactive dyes with vinylsulfone anchors (PVS-TPDO) and monochlorotriazine anchors (MCT-TPDO) were investigated in water, in aqueous organic solvent, and on a cellulosic substrate. The aggregation tendency of PVS-TPDO in water was promoted by the addition of neutral electrolyte and suppressed by that of 1-methyl-2-pyrrolidone (MP). The dimerization constants, K, for PVS-TPDO were estimated in water and in aqueous sodium chloride solution; PVS-TPDO showed also aggregation on a cellulosic substrate. The apparent value of K on dry cellulose was two orders of magnitude smaller than that in water, and was increased by about ten times by water. The aggregation of PVS-TPDO in aqueous sodium chloride solution was suppressed by the addition of both MP and poly(vinylpyrrolidone). Four TPDO dyes examined showed the same order of aggregation tendency on cellulosic and nylon substrates as that in aqueous solution. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive dye; Triphenodioxazine dye; Vinylsulfonyl anchors; Monochlorotriazinyl anchors; Aggregation

1. Introduction

The aggregation of dyes is well known to have a strong influence on the dyeing process. The phenomenon has been extensively studied over many years but has provided diverse results containing some discrepancies [1–6]. In the case of C.I. Direct Blue 1, the activity coefficients of the dye in aqueous solution were found to be those expected for a normal strong electrolyte, a fact that suggests that the dye dissolves in water as a single molecule [7]. Similar results were obtained for the two acid dyes, C.I. Acid Orange 7 and C.I. Acid Orange 8 [8]. There is a considerable amount of evidence to show that dye molecules form aggregates in aqueous solution at room temperature to an extent that depends on their molecular size and the number of solubilizing groups [1–6]. The size of the dimers, trimers, etc. is likely to be such as to exclude them from entering the fiber. The extent of dye aggregation decreases as the temperature is raised and more of the monomeric form is liberated [9]. Direct dyes such as Congo

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Red, Ben-zopurpurine 4B, etc. have been taken as indicating an extreme situation, since such dyes were found to form micelles of a certain size and their solutions show a well-defined, critical micelle concen-tration [1–3,10,11]. Thus, broad generalizations have been established regarding dye aggregation behavior [3]. Aggregation increases with increase in dye concentration and increase in ionic strength, as well as by the introduction of alkyl chains into the dye molecule because of increased hydrophobic interaction in solution. Aggregation decreases with the addition of organic solvents and by the introduction of ionic solubilizing groups such as sulfonic acid groups. At present, however, it is considered that the hydrophobic effect is unlikely to play a significant role in anionic, azo dye aggregation [3]. The present under-standing of the relationship between dye structure and behavior in aqueous solution is far from complete.

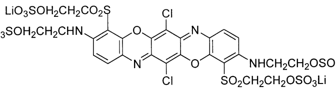
The authors could not find any systematic study on the aggregation behavior of dyes for a particular dye under various environmental conditions. In preliminary experiments on triphenodioxazine reactive dyes, some dyes with a high tendency to aggregate were found in aqueous solution as well as on cellulosic substrate. In this paper, the aggregation behavior of TPDO reactive dyes has been examined in aqueous solution in both the presence and absence of electrolyte as well as in aqueous, organic solvent and on both cellulosic and nylon substrates.

2. Experimental

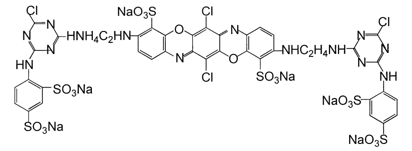
2.1. Dyes

According to Renfrew [12] and Zollinger [13], TPDO reactive dyes differ only in the substituents and their positions in the TPDO ring. C.I. Reactive Blue 187 (C.I. 51307) is the only commercial TPDO reactive dye whose chemical structure has been disclosed [13]. The dyes used in the present study possess reactive and solubilizing groups at the 3-, 4-, 10- and 11-positions. Four, typical TPDO dyes were selected and synthesized according to the procedure described in patent literature. The structures of the dyes used are shown below as well as the abbreviations used and the corresponding patents.

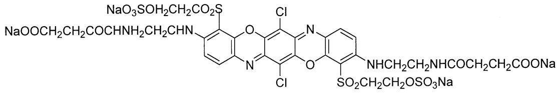
(1) A triphenodioxazine dye with two vinylsulfone anchors (PVS-TPDO) [14].



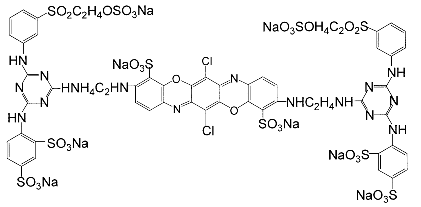
(2) A triphenodioxazine dye with two monochlorotriazine anchors (MCT-TPDO) [15].



(3) A triphenodioxazine dye with two vinylsulfone anchors (VS-TPDO) [16].



(4) A triphenodioxazine dye with two vinylsulfone anchors through a triazine ring (BF-TPDO) [17].



All chemicals used were of reagent grade and were used without further purification.

2.2. Methods

2.2.1. Purification

The dyes synthesized were isolated by pouring the aqueous reaction solution into a 30- to 60-fold excess of acetone. After 30 min stirring, the precipitates were filtered and washed with a small amount of methanol. Further dye purification of PVS- and

MCT-TPDO was achieved by preparative HPLC, using a reverse phase C18 silica gel column. Finally, to minimize the content of electrolyte such as sodium or lithium sulfate and chloride, reverse osmosis was used, since the association of TPDO's is highly sensitive to the electrolyte concentration but less so to dye concentration.

2.2.2. *Dyeing of cellophane*

Cellophane films (Futamura Kagaku Kogyo K.K., # 300, thickness of a sheet of dry cellophane = 19.0 μm (original) and 20.5 μm (after scouring)), cut into tapes of 3 cm wide in the direction of length, or were dyed at pH 9.0 (using Na_2HPO_4) for between 1 h (pale) and > 4 h (deep) were treated in an aqueous alkaline solution (Na_2CO_3, 20 g dm^{-3}; Na_2SO_4, 50 g dm^{-3}), for < 90 min after equilibrium adsorption for > 60 min (alkali-shock method) to obtain the prescribed depth at 50°C for VS dyes or at 80°C for MCT dyes. After dyeing, wash-off was carried out to remove unfixed dye by repeatedly treating the dyeings in boiling water for 1 h until the wash solution was uncoloured. Whether or not both the reactive groups of TPDO's reacted with cellulose was not examined.

2.2.3. *Dyeing of nylon film*

Biaxially stretched nylon 6 film (Emblem®) obtained from Unitica Ltd., of thickness 25 μm, was cut into tapes of 3 cm wide. The tapes were dyed at pH 3 to obtain the required depth at 70°C for the VS dyes and at 80°C for the MCT dyes, and then dye fixation was achieved by treating in phosphate buffer (0.01 M Na_2HPO_4 + 0.01 M NaH_2PO_4, pH 6.9) for 1 h. Wash-off was carried out by repeatedly treating in water for 1 h at 80°C until the wash solution was uncoloured.

3. Results and discussion

3.1. *Aggregation of PVS-TPDO in aqueous solution*

3.1.1. *Calculation of dimerization constants*

In the aggregation equilibrium between monomer, D and *n*-mer, D_n:

$$nD \rightleftarrows D_n \tag{1}$$

the aggregation constant, *K*, is given by Eq. (2) [20]:

$$K = \frac{x}{nC_0^{n-1}(1-x)^n} \tag{2}$$

where *n* denotes the aggregation number, $1-x$ and x/n are the fractions of monomer and *n*-mer, respectively, and C_0 is the analytical concentration of dye.

The absorption spectra of PVS-TPDO in aqueous solution were measured at different concentrations in the absence of neutral electrolyte and are illustrated in Fig. 1; the values of ε (molar extinction coefficient) at λ_{max} are shown. The spectra of PVS-TPDO showed an isobestic point that may indicate the monomer-dimer equilibrium. The dimerization constant, *K* (dm^{-3} mol), was calculated by the method of Zanker [20]; the aggregation number was estimated to be 2.1, which is consistent with the existence of the isosbestic point. In the present study, by using an observed value, the apparent molar extinction coefficient, ε, for the dye solutions of different concentrations at λ_{max}, the values of *K* were calculated using Eq. (2). The value of molar fraction of dimer, *x*, was determined using Eq. (3).

$$\varepsilon = \frac{\varepsilon_2}{2}x + (1-x)\varepsilon_1 \tag{3}$$

where ε_1 and ε_2 are the molar extinction coefficients for the monomer and dimer, respectively, whose ratio $\varepsilon_2/\varepsilon_1$ was estimated by the Zanker method [20].

3.1.2. *Dimerization constant*

The aggregation of PVS-TPDO in aqueous solution as expressed by the values of *K* , is shown in Table 1, together with the results for the metal-free phthalo-cyanine disulfonate sodium salt (disulfo-Pc) [19]. Since metallisation of phthalocyanine (Pc) enhances the extent of interaction between the Pc rings without changing the geometry of the dimer [21–23] and sulfonation markedly lowers interaction (cf. Table 2), the values of K for PVS-TPDO may be comparable to those for Pc's.

In order to compare the values of K in water among various dyes, the values for typical dyes were collected and expressed as Gibbs free energy [$\Delta G = -RT \ln K$ (kJ mol^{-1})] in Table 2. The values of K for five basic dyes and two anionic monoazo dyes, which were listed by Coates [2], range from 10^3 to 10^4 at 25°C. Copper phthalocyanine (Cu-Pc) dyes are known to have a high aggregation tendency in the dyebath [18]. Disulfo-Pc in aqueous solution has an isosbestic point that identifies a monomer–dimer equilibrium and a further isobestic point at a higher concentration that indicates a dimer–tetramer equilibrium [19].

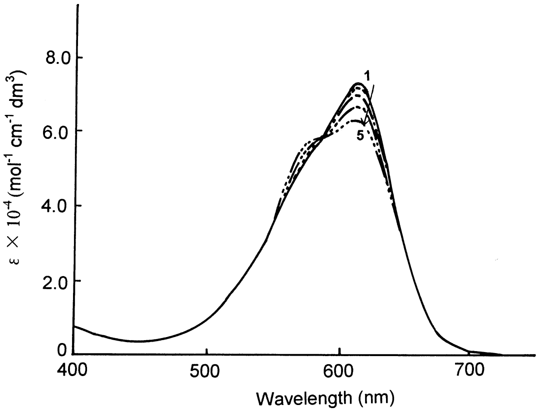


Fig. 1. Absorption spectra of PVS-TPDO in aqueous solution at different dye concentrations: 1, 2.46×10^{-6}; 2, 5.31×10^{-6}; 3, 1.06×10^{-5}; 4, 2.12×10^{-5}; 5, 4.24×10^{-5} mol dm^{-3} at 25°C (isosbestic point = 587.0 nm, $\lambda_{max} = 613$ nm, $\varepsilon = 7.28\times10^4$ mol^{-1} dm^3 cm^{-1}) (cf. Table 1).

According to Schnabel et al. [19], disulfo-Pc exists as fractions of monomer, dimer and tetramer in aqueous solution, which are estimated by the values of K and K' (the aggregation constant between dimer and tetramer) (cf. Tables 1 and 3). Considering the aggregation tendency in terms of dimerization constant, the value of K for PVS-TPDO in water was one thousandth as small as that for disulfo-Pc. The spectral variation of PVS-TPDO with dye concentration were smaller than those of disulfo-Pc [19].

As with disulfo-Pc, the fraction of the dimer of PVS-TPDO was calculated from the values of K and the results are listed in Table 3. When compared with that of disulfo-Pc, the very small aggregation tendency of PVS-TPDO is indicated by the fraction of the dimer.

PVS-TPDO has a large, rigid and planar structure of high symmetry and has a dimerization constant of magnitude similar to that of dyes with known high aggregation tendency [1–5] (cf. Table 2). Although the general aggregation behaviour of reactive dyes is not known due to a lack of consistent data for reactive dyes, the aggregation behavior of this dye may be considered as being typical of that of ionic dyes.

3.1.3. *Effect of sodium chloride on aggregation*

The effects of adding sodium chloride to aqueous solutions of PVS-TPDO are shown in Fig. 2; the presence of an isosbestic point implies the existence of a mono-mer-dimer equilibrium. The position of the isosbestic point in Fig. 2 virtually coincides with the isosbestic point in Fig. 1,

Table 1
Dimerization constants, K ($=[D_2]/[D]^2$) (mol^{-1} dm^3), for PVS-TPDO, MCT-TPDO, and metal-free disulfo-phthalocyanine (disulfo-Pc) [19] in aqueous solutions containing sodium chloride

Temperature	PVS-TPDO (NaCl g dm^{-3})		MCT-TPDO (NaCl g dm^{-3})		Disulfo-Pc (no salt)
25°C	3.8×10^3	(0.0)	0^a	(0.0)	6×10^6
	7.3×10^3	(1.0)	5×10^2	(1.0)	
	2.2×10^4	(2.0)	4×10^3	(10.0)	($K' = 5\times10^4$ mol^{-2} dm^6)^b
	4.6×10^4	(5.0)	2×10^4	(50.0)	
	1.4×10^5	(10.0)	5×10^4	(100.0)	
40°C	6.8×10^4	(10.0)			
50°C	3.5×10^4	(10.0)			

[a] Beer's law held up to the concentration of 1.7×10^{-4} mol dm^{-3}.

[b] The aggregation constant between dimer and tetramer.

Table 2
Thermodymamic parameters of dimerization for some dyes in aqueous solution

Dyes	Temp.(°C)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	Ref.
Metal-free disulfo-Pc	25	−38.7	–	–	[19]
C.I. Direct Blue 86[a] (Cu disulfo-Pc)	27[c]	−34.6	−42.5	−26.0	[6,24]
Cobalt tetrasulfo-Pc	38	−33.6	−58.8	−75.6	[25]
C.I. Reactive Blue 7[b]	27[c]	−32.5	−26.0	21.5	[6,24]
PVS-TPDO (NaCl: 10 g dm^{-3})	25	−29.4	−43.8	−48.2	This study
C.I. Reactive Blue 7 (hydrolyzed)	27[c]	−28.5	−63.5	−116.7	[6,24]
Acridine Orange	23	−24.1	−37.4	−41.3	[26]
C.I. Basic Blue 41	25	−23.3	−17.9	17.1	[27]
C.I. Reactive Violet 4	25	−21	–	–	[10]
PVS-TPDO (no salt)	25	−20.4	–	–	This study
C.I. Acid Red 88	25	−19.3	−55.2	−120.4	[28]
C.I. Acid Red 14	20	−11.9	−17	−18	[29]

[a] C.I. 74180.
[b] C.I. 74460.
[c] From the data given [6,24], the temperature was estimated to be 300 K.

Table 3
Molar fraction of the monomer (D), dimer (D_2), and tetramer (D_4) for disulfo-Pc [19], PVS- and MCT-TPDO in aqueous solution (25°C)

Dye	Disulfo-Pc			PVS-TPDO						MCT-TPDO			
Concentration of NaCl	0 g dm^{-3}			0 g dm^{-3}		2.0 g dm^{-3}		10.0 g dm^{-3}		10.0 g dm^{-3}		50.0 g dm^{-3}	
Oligomer	D	D_2	D_4	D	D_2	D	D_2	D	D_2	D	D_2	D	D_2
10^{-6} dye mol dm^{-3}	0.25	0.75	0	0.993	0.007	0.96	0.04	0.81	0.19	0.992	0.008	0.96	0.04
10^{-4} dye mol dm^{-3}	0.02	0.94	0.04	0.66	0.34	0.38	0.62	0.17	0.83	0.66	0.34	0.39	0.61
10^{-2} dye mol dm^{-3}	0	0.24	0.76	0.11	0.89	0.05	0.95	0.02	0.98	0.11	0.89	0.05	0.95

although the absorption spectra of this dye were highly sensitive to a change of environment, as discussed later. An increase in the concentration of dimer brought about a descent of the main absorption band and an ascent of a shoulder of the main absorption band on the shorter wavelength side, an apparent blue shift. The addition of an electrolyte resulted in typical spectral variations of dimerization.

If sodium chloride was assumed to have no effect on the molar extinction coefficients of monomer and dimer for PVS-TPDO, an increase in the aggregation constants for PVS-TPDO with an increase in the concentration of electrolyte can be estimated (Table 1). The aggregation of PVS-TPDO was highly sensitive to the electrolyte concentration because, perhaps, the added electrolyte lowered the electrostatic repulsion between anionic groups or decreased Debye length, as a consequence of which, the values of K for this dye were similar to that of disulfo-Pc in water (cf. Table 2). As this dye may predominantly exist as dimers in a dyebath that contains an electrolyte, the electrolyte sensitivity of aggregation tendency for this dye may be high like that of the other anionic dyes.

In practice, however, since the sulfatoethylsulfonyl groups in PVS-TPDO are converted to vinylsulfonyl groups under the alkaline fixation conditions, the values of K for the vinylsulfonyl form of the dye may increase [6,24] and be further increased by electrolyte addition.

3.1.4. Temperature effect on aggregation

The absorption spectra of PVS-TPDO in aqueous solution containing an electrolyte were effected, considerably, by changes in temperature (Fig. 3). If the change in the molar volume of solution with temperature is neglected, the values of K can be calculated by the change of ε at λ_{max} as shown in Table 1. An increase in temperature of 10°C reduced the values of K by some 50%.

Thermodynamic parameters for the dimerization of PVS-TPDO in aqueous solution were estimated from the values of K at different temperatures. The estimated values (Table 2) show that PVS-TPDO has an aggregation tendency comparable to that of typical commercial dyes with a high aggregation tendency. Although previous workers have emphasized the contribution of hydrophobic interaction to dimerization [4,5], only a rough compensation effect between the entropy and enthalpy terms seems to exist, even if the cratic term is taken into consideration. An increase of the enthalpy term contribution is also notable with a rise in aggregation tendency as it is emphasized in the aromatic interaction in molecular aggregation [22,23] (cf Section 3.4.3.).

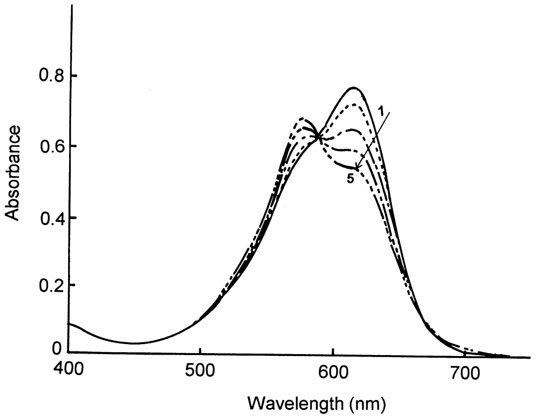


Fig. 2. Absorption spectra of PVS-TPDO in aqueous solution containing different concentrations of sodium chloride: 1, 0; 2, 1.0; 3, 2.0; 4, 5.0; and 5, 10.0 g dm^{-3} at 25°C (dye = 1.06×10^{-5} mol dm^{-3}, isosbestic point = 587.0 nm and λ_{max} = 613 nm) (cf. Table 1).

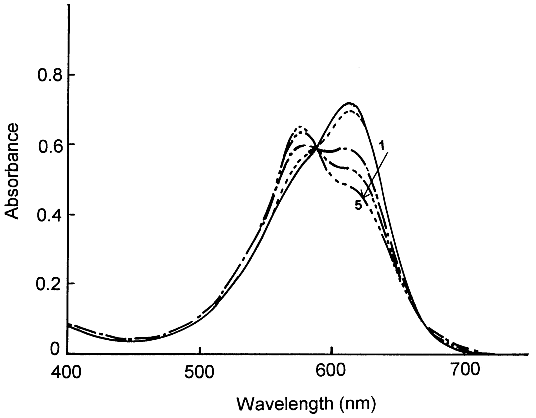


Fig. 3. Temperature effect on the absorption spectra of PVS-TPDO (9.93×10^{-6} mol dm^{-3}) in aqueous sodium chloride solution. No salt: 1, 50°C (λ_{max} = 613 nm); 2, 25°C, and 10.0 g NaCl dm^{-3}: 3, 50°C; 4, 40°C; 5, 25°C (cf. Table 1).

3.1.5. *Influence of organic solvent*

To examine any solvent-induced spectral changes, the absorption spectra of PVS-TPDO in aqueous 1-methyl-2-pyrrolidone (MP) solution were measured (Fig. 4). It is evident that as MP content increased, λ_{max} underwent a red shift followed by a gradual blue shift (at > 20% MP). The TPDO dyes had no isosbestic point in the presence of organic solvents such as MP and DMF unlike

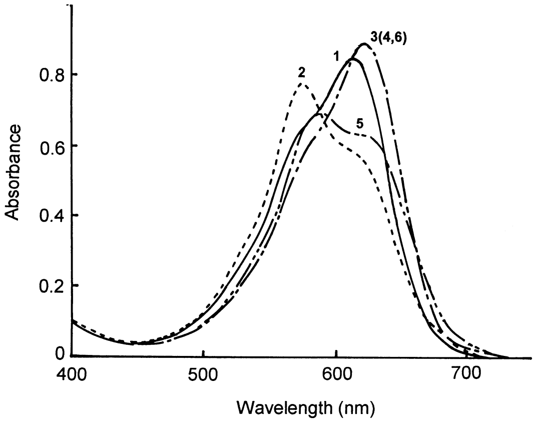


Fig. 4. Absorption spectra of PVS-TPDO (dye = 1.22×10^{-5} mol dm^{-3}) in aqueous MP solution containing sodium chloride at 25°C.

	Water	Aqueous 20% (v/v) MP solution	Aqueous PVP[a] solution	
			5.0 g dm^{-3}	10.0 g dm^{-3}
No salt	1	3[b]	–	–
10 g dm^{-3} NaCl	2	4[b]	5	6[b]

[a] Albigen A.

[b] The spectrum for the three solutions (spectra 3, 4, and 6).

other dyes such as Cu-Pc [29], basic dyes [30], etc., since the absorption spectrum of this dye was sensitive to the change of environment.

The disaggregating effect of MP is shown by the spectral variation depicted in Fig. 4. When compared with the spectrum obtained in water, the spectra in aqueous 20% MP solution had a smaller shoulder on the shorter wavelength side. The addition of MP to an aqueous, electrolyte solution of PVS-TPDO imparted a hyperchromic change and a shift in λ_{max}. However, the absorption spectra of PVS-TPDO in aqueous 20% MP solution in both the presence and absence of sodium chloride were identical. The addition of MP to an aqueous, electrolyte solution of PVS-TPDO clearly had a disaggregating effect. Since aqueous MP solutions of dye have no isosbestic point and the values of ε_1 and ε_2 may change with MP content, the aggregation of TPDO dyes in aqueous MP solution can be treated only qualitatively from the shape of spectrum. Organic solvents such as MP and dimethylformamide are regarded to disaggregate dimerised dyes in aqueous solution [5]. This effect can be attributed to a lowering of the dielectric constant of the medium which strengthens the dipolar interactions [22,23].

3.1.6. *Effect of polyvinylpyrrolidone*

The interaction between a dye and a polymer in aqueous solution results in so-called metachromasia [5], from which the binding modes of the dye molecules on the polymer can be analyzed. Weingarten [18] and Baumgarte [32] reported the effects of dyeing assistants added to the dyebath on the absorption spectra of dyes. The addition of polyvinylpyrrolidone (PVP) to the dye solution had hyperchromic and red shift effects, these being similar to those observed for MP in this work. The apparent disaggregating effect on PVS-TPDO by PVP was further confirmed by adding it to an aqueous dye solution containing sodium chloride (Fig. 4, Spectra 5 and 6). In the case of a small addition of PVP, the spectrum (5, Fig. 4) showed only a decrease in the dimer fraction; however, the addition of a large amount of PVP caused the spectrum to coincide with that of an aqueous 20% MP solution. In the case of the solution (10^{-5} mol dm^{-3}) without PVP and MP, about 50% of the dye may exist as the dimer. When PVP is added, PVS-TPDO may be bound to PVP in the aqueous phase, which has an apparent disaggregating effect on the spectrum [5]. The absorption spectra correspond to those for PVS-TPDO bound with PVP, implying that the dyes were mono-molecularly bound with PVP, which may be expressed by the following equilibrium (non-stoichiometric):

$$\underset{\text{On polymer}}{\mathrm{PVP}-(\mathrm{D})_n} \rightleftarrows \underset{\text{in solution}}{\mathrm{D} \rightleftarrows \mathrm{D}_2} \qquad (4)$$

PVS-TPDO may not be adsorbed on or bound to PVP as the dimer. Thus, the dimer of PVS-TPDO has a smaller affinity for PVP than has the monomer [32]. Since the amount of the monomer in solution diminishes due to the adsorption on PVP, the concentration of dimer, which dissaggregates to keep the monomer–dimer equilibrium, is reduced as a consequence. This is well expressed by the different spectral changes caused by small and large additions of PVP. In general, similar situations may hold for the adsorption of anionic dyes on cellulose, even when some aggregates exist in the dyebath [32]. In the case of PVS-TPDO, some proportion of the dimers and the monomers are adsorbed by cellulose, although small fractions of monomer exist in the dyebath to which large amounts of electrolyte have been added.

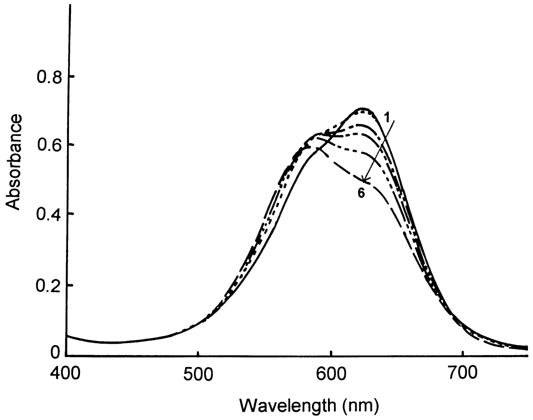


Fig. 5. Absorption spectra of MCT-TPDO in aqueous solution containing different concentrations of sodium chloride: 1, 0; 2, 1.0; 3, 10.0; 4, 20.0; 5, 50.0, and 6, 100 g dm^{-3} at 25°C (dye = 1.73×10^{-5} mol dm^{-3}, $\lambda_{max} = 625$ nm) (cf. Table 1).

3.2. Aggregation of MCT-TPDO in aqueous solution

In the absence of an electrolyte, MCT-TPDO manifested no aggregation, from which it can be concluded that this particular dye has a very much smaller aggregation tendency than PVS-TPDO. Fig. 5 clearly shows that large amounts of electrolyte were needed to promote aggregation. The resulting spectra resemble those of Thionine at pH 3.5 [31] in shape showing the monomer–dimer equilibrium; isosbestic points seem to exist around 680 and 580 nm. Assuming the existence of monomer–dimer equilibrium, the dimerization constants were calculated as before using the absorbance at $\lambda_{\max}$ of this dye in water without electrolyte (Table 1). The aggregation of MCT-TPDO in aqueous solution to which 50 and 100 g dm^{-3} of sodium chloride were added corresponds to that of PVS-TPDO in aqueous solution to which 2 and 5 g dm^{-3} of sodium chloride were added, respectively. The effect of electrolyte on the aggregation of MCT-TPDO is about one twentieth as small as that for PVS-TPDO. Besides the number of sulfonic acid groups present in the two dyes, the essential reason for such a marked difference in aggregation remains to be determined.

3.3. Aggregation tendency of VS- and BF-TPDO

By utilizing the experimental results obtained above, the aggregation tendency of VS- and BF-TPDO can be estimated and the aggregation tendency among the four dyes can be assessed. As the dyes have a common parent structure, they may have molar extinction coefficients of the same order. To obtain aqueous dye solutions of similar absorbance, dye solutions of molar concentration ca 10^{-5} mol dm^{-3} were prepared. As the samples taken must be proportional to the molecular weight of the dye, it was confirmed that the dyes contained nearly similar contents of electrolyte (less than 10% by mass). When adding sodium chloride at more than 1 g dm^{-3} to the solution, the amount of electrolyte originally present in the dyes can be neglected.

Assuming that there is a close correlation between the extent of aggregation and ionic strength, it is possible to compare the aggregation tendency of the four TPDO dyes. The spectral variations of VS- and BF-TPDO caused by the addition of NaCl and MP are illustrated in Fig. 6(a) and (b), respectively. The shape of the absorption spectra and the presence of an isosbestic point implies the existence of monomer–dimer equilibrium for VS-TPDO and indicates that the dye exists predominantly as the dimer in aqueous electrolyte solution [Fig. 6(a)]. The dimer band showed a blue shift that was accompanied by a deviation from the isosbestic point upon addition of the electrolyte in excess of ca 10 g dm^{-3}. Alternatively, BF-TPDO displayed an isosbestic point in the presence of up to ca 60 g dm^{-3} electrolyte [Fig. 6(b)]. Further addition of electrolyte in excess of ca 100 g dm^{-3} caused the dimer band to experience a blue shift that was accompanied by a deviation from the isosbestic point as observed for VS-TPDO. The deviation from the isosbestic point may be due to the formation of larger aggregates

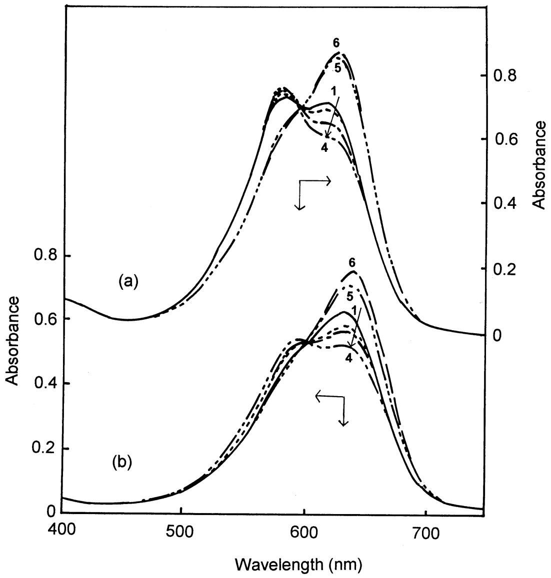


Fig. 6. Variations of absorption spectra of (a) VS-TPDO by the salt addition at the concentrations: 1, no salt; 2, 1.0; 3, 2.0; 4, 5.0 g NaCl dm^{-3} (isosbestic point = 589.5 nm) and in the aqueous solution of MP contents: 5, 15; and 6, 25 %(v/v) ($\lambda_{\max}$ = 624 nm), and (b) BF-TPDO by the salt addition at the concentrations: 1, no salt; 2, 20.0; 3, 40.0; 4, 60.0 g NaCl dm^{-3} (isosbestic point = 602.0 nm) and in the aqueous solution of MP contents: 5, 10; and 6, 20%(v/v) ($\lambda_{\max}$ = 638.5 nm).

due to dimer–dimer interactions. From the concentration effect of electrolyte on the absorption spectra illustrated in Fig. 2 and Fig. 6(a), the aggregation tendency of VS-TPDO can be judged to be larger than that of PVS-TPDO. Comparing the same effects for the spectra of BF-TPDO [Fig. 6(b)], PVS-TPDO (Fig. 2), and MCT-TPDO (Fig. 5), the order of aggregation tendency of the four dyes examined may be as follows:

$$\begin{aligned}&\mathrm{VS-TPDO > PVS-TPDO >}\\ &\mathrm{BF-TPDO > MCT-TPDO}\end{aligned} \tag{5}$$

This tendency was further confirmed by increasing the amount of MP added to the dye solution as shown in Fig. 6(a) and (b). A hyperchromic shift of BF-TPDO was observed that was accompanied by a slight decrease of the shoulder on the short wavelength side of the main band at $\geqq$10% MP, while no hyperchromic shift of VS-TPDO was observed. With increasing addition of MP to the aqueous solution, the aggregation of VS-TPDO was reduced to give complete disaggregation at $>$20% MP, while dissaggregation of BF-TPDO was attained at $\leqq$10% MP. This fact supports also the conclusion mentioned above.

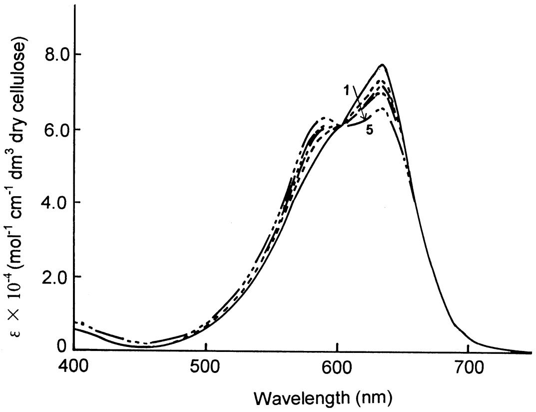


Fig. 7. Absorption spectra of PVS-TPDO of different concentrations on dry cellophane: 1, 1.77×10^{-3}; 2, 3.36×10^{-3}; 3, 7.31×10^{-3}; 4, 8.30×10^{-3}; 5, 1.97×10^{-2} mol kg^{-1} (isosbestic point = 601.0 nm). Ordinate: estimated value of ε (mol^{-1} cm^{-1} dm^3 dry cellulose) (see text).

3.4. *Dimerization on cellophane film*

3.4.1. *Aggregation of PVS-TPDO on dry cellulose*

In order to confirm the aggregation of PVS-TPDO on cellulose, cellophane films were dyed with PVS-TPDO. Assuming a similarity in absorption spectra in aqueous solution and on cellophane, the isosbestic point on cellophane was estimated to be 601 nm. An assumption that this dye has the same values of ε at the isosbestic points in water and on dry cellulose was made. Fig. 7 shows that up to high dye concentration [the absorbance of dyed cellophane (thickness: 20.5 μm) at $\lambda_{\max}$ ca 2.5], the absorption spectra seemed to be unchanged, implying the existence of monomer–dimer equilibrium. This fact may support the assumption of linearity in ε at the isosbestic point in different solutions.

The proportion of the dimer increased with increase in the total dye concentration, since the shoulder of the main band on the short wavelength side became larger with an increase in dye concentration. However, a slight blue shift of $\lambda_{\max}$ was observed at very high dye concentration. When the heterogeneity of the inner structure of the cellulosic film is ignored, an apparent value of K in the unit volume of dry cellulose was estimated to be ca 10 (mol^{-1} dm^3 dry cellulose) by use of the absorbance at $\lambda_{\max}$. A small apparent value of K on dry cellulose was obtained in spite of a distinct aggregation tendency on cellulose. If the dyes on dry cellulose are assumed to exist homogeneously, ca 20 % of them are estimated to form dimer in a high concentration (2.0×10^{-2} mol dm^{-3} dry cellulose). However, PVS-TPDO on cellulose has a smaller number of solubilizing groups than when in aqueous solution and is covalently bound to the cellulose. Hydrolysis of reactive groups is well known to influence aggregation tendency of reactive dyes [6,24] (cf. Table 2).

3.4.2. *State of existence of TPDO dyes on the substrate*

The absorption spectra of four TPDO reactive dyes examined on dry cellulosic and nylon films are shown in Fig. 8(a) and (b), respectively. From the aggregation tendency of the four dyes determined above (cf. Section 3.3), those dyes of

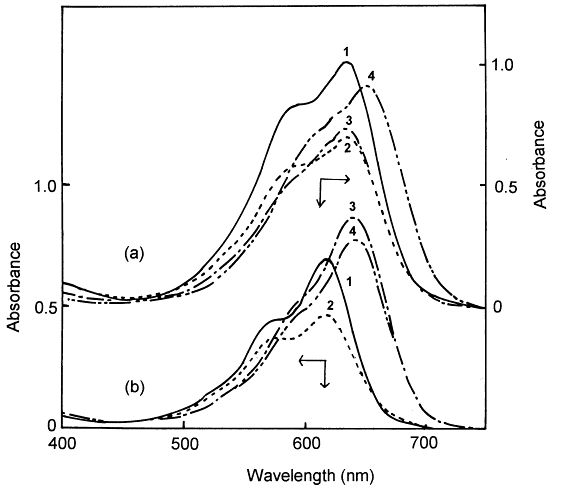


Fig. 8. Absorption spectra (as measured) of TPDOs on (a) dry cellophane and (b) nylon film: 1, PVS-TPDO (spectrum 1 on cellophane corresponds to spectrum 3 in Fig. 7); 2, VS-TPDO; 3, MCT-TPDO, and 4, BF-TPDO.

high aggregation tendency in aqueous solution yielded only pale depths of shade on nylon. In the case of cellulose, the spectrum of PVS-TPDO (cf. figure caption) was used as a reference. From the ratios of absorbance at $\lambda_{\max}$ for the monomer and dimer forms, the aggregation tendency of the dyes was compared. The spectra show that these dyes exist partially as dimers on both substrates. From these results, two distinct features were observed:

1. In terms of the aggregation tendency of the dyes on cellulosic and nylon substrates:

$$\begin{aligned} &\mathrm{VS-TPDO} > \mathrm{PVS-TPDO} > \\ &\mathrm{BF-TPDO} > \mathrm{MCT-TPDO} \end{aligned} \tag{6}$$

2. The aggregation tendency on the substrates: cellulose ÷nylon.

From a comparison of (5) and (6), it appears that the aggregation tendency of TPDO dyes on cellulosic and nylon substrates is the same as that in aqueous solution. However, as mentioned below (cf. Section 3.4.4), when the similarity in aggregation tendency in water and on the two substrates is compared for dyes with different parent structures, the similarity may not hold.

On nylon, the aggregation behaviour of the TPDO dyes seems to be similar to or lower than that on cellulose, although the effects of concentration difference between the substrates were not taken into consideration. No clear difference was found between the absorption spectra for each dye on the cellulosic and nylon substrates, although the differences in the absorption spectra varied with dyes. MCT-TPDO may exist almost only as a monomer on both substrates. VS- and PVS-TPDO seem to display aggregation behaviour on the nylon film. However, since it was difficult to compare which substrate was larger because of the differences in absorption spectra between the substrates and among the dyes, it was estimated qualitatively to be nearly the same.

3.4.3. Aggregation on water-swollen cellulose

Assuming the similarity in absorption spectra for a dye in aqueous solution and on cellophane film, the isosbestic point on cellophane was estimated to be 604 nm. The absorption spectra of PVS-TPDO on water-swollen cellulose (the same films as used in Fig. 7) are shown in Fig. 9. They dramatically changed in shape by swelling, indicating an increase in dimerization.

From the relative height of the double peak of the main band, it was concluded that the molar extinction coefficients of this dye at different wavelengths

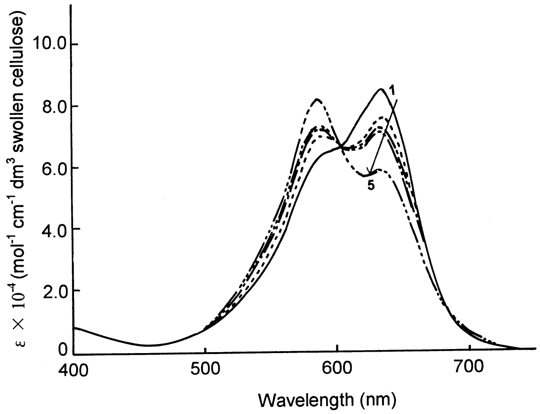


Fig. 9. Absorption spectra of PVS-TPDO at different concentrations on water-swollen cellophane, the same dyed cellophane films as used in Fig. 7 (isosbestic point = 604.0 nm). Ordinate: estimated value of ε (mol^{-1} cm^{-1} dm^{3} swollen cellulose) (see text).

on the water-swollen cellulose might be different from those in aqueous solution and on dry cellulose. Although the degree of swelling of the dyed cellophane was not so different from that of the original cellophane [33], the fact that a larger proportion of dimer was present on the water-swollen cellulose than on the dry cellulose is evident from the shape of the absorption spectra. The proportions of dimer at high depth of shade were estimated to be 50% from the absorbance at $\lambda_{\max}$, assuming linearity in the value of ε at the isosbestic points, having taken the volume change by swelling into consideration. The apparent value of K in the unit volume of water-swollen cellulose is ca 100 (mol dm^{-3} swollen cellulose). Besides the effect of water, the dilution effect due to volume expansion can also be considered to contribute to the increase in dimerization constant observed for the swollen substrate.

Although precise estimation is impossible as mentioned above, the aggregation tendency of this dye was increased considerably by swelling. However, the aggregation behaviour of PVS-TPDO in swollen cellulose is still considerably smaller than that in water. Despite the heterogeneous distribution of dye in the cellulosic substrate, existence of counter ions in a high concentration as well as that of water may promote the dimerization on cellulose. Thus, since penetration of water of large dielectric constant into the dyed cellulose diminishes the long-range coulombic repulsion operating between TPDO molecules but, at the same time, increases the short-range polar interactions which contrasts to the addition of organic solvents with smaller dielectric constant, swelling of cellulose by water might promote dye aggregation. Immersion of the sample in aqueous electrolyte solution (0.01~1M NaCl) showed no change in the spectra in water probably due to the existence of counter ions of dye in the cellulose. The presence of counter ions in high concentration might lessen the influence of electrolyte addition.

Suzuki and Tsuchiya [34] reported the promotion effect of pressure on the aggregation of basic dyes in aqueous solution. These workers ignored the contribution which hydrophobic interaction may make towards dye aggregation from this effect, ansd suggested hydrogen bonding as the main binding force in the aggregation of dyes. Dispersion force and an increase in the dielectric constant of water with increasing pressure are supposed to assist this aggregation.

The absorption spectra of PVS-TPDO seem to be determined by the concentration of dye on the cellophane, independently of the method of dyeing. However, alkali-shock dyeing (as practised here) in the presence of large amounts of electrolyte in the dye adsorption stage, seems to result in dyeings with a larger proportion of aggregates. In general, exhaustion dyeing or equilibrium adsorption gives a state of dye adsorption with a large proportion of dimmers and dyeings of a violet color. Simultaneous dye adsorption and fixation in the presence of a large amount of electrolyte resulted in similar dyeings. After thorough wash-off in boiling water, royal blue dyeings with a smaller proportion of dimers were obtained. Thus, the value of K for PVS-TPDO on cellulose may not be an absolute. The TPDO dyes other than PVS-TPDO with some tendency to aggregate showed similar behavior to each other.

3.4.4. *Influence of MP on the aggregation of PVS-TPDO on cellulose*

Using the method described previously [30], the absorption spectra of PVS-TPDO on cellophane films were measured by immersing the dyed film in aqueous MP solution as shown in Fig. 10. Since no reduction of film thickness occurred, the

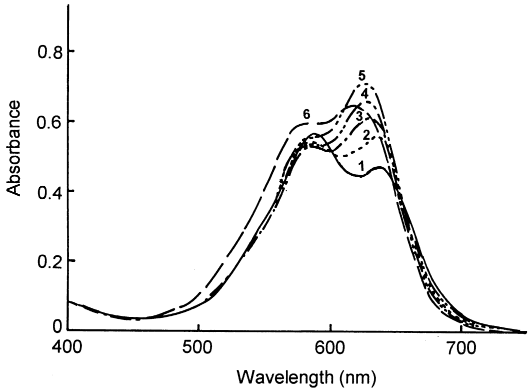


Fig. 10. Absorption spectra of PVS-TPDO (as measured) (3.60×10^{-3} mol kg^{-1} dry cellulose) on cellophane immersed in aqueous solution: 1, water; 2, 50 %(v/v) MP; 3, 70% (v/v) MP; 4, 80% (v/v) MP; 5, 95 %(v/v) MP; and 6, 100 %(v/v) MP.

hyperchromic effect is real. Unlike the case of Cu-Pc on cellulose immersed in aqueous dimethylformamide (DMF) solution [30], water promoted the aggregation of PVS-TPDO on cellulose by swelling (cf. 3.4.3). It is interesting to note that the swelling, in water, of cellulose film which had been dyed with vinylsulfonyl, Cu-Pc reactive dyes, resulted in no change of absorption spectrum in shape; whilst the dimer of Cu-Pc exists to some extent on dry cellulose, the aggregation is not promoted by immersion in water. These facts suggest that PVS-TPDO has a greater propensity to aggregate on the cellulosic substrate.

Immersion of the dyed film in aqueous MP solution resulted in complex spectral shifts in the absorption spectra of PVS-TPDO (Fig. 10). The shoulder present on the shorter wavelength side of the main absorption band for PVS-TPDO on water-swollen film became a peak when immersed in aqueous MP solution, showing the existence of dimers. The dimer peak decreased with an increase in the concentration of MP, returning to the spectrum observed on dry film, which was characteristic of a monomer-predominant mixture of monomer and dimer. The addition of MP to the aqueous solu-tion promoted the disaggregation of PVS-TPDO on the cellulosic substrate. Immersion in pure MP as well as DMF, however, caused the dyed cellophane to become brittle and had only a small disaggregating effect. Incomplete disaggregation of PVS-TPDO on water-swollen cellulose by the addition of organic solvents implies a high aggregation tendency.

3.4.5. Reversibility of absorption spectra on cellulose

The absorption spectra of PVS-TPDO on cellulosic film changed in shape depending upon whether the film was dry, immersed in water or in aqueous MP solution. The change in absorption spectra was reversible, regardless of the history of the sample.

4. Summary

PVS-TPDO has an aggregation tendency in aqueous solution which is promoted by the addition of an electrolyte and suppressed by that of MP. The absorption spectra of PVS-TPDO are sensitive to the environment accompanied with a shift of $\lambda_{\max}$. The dimerization constant, K, for PVS-TPDO is of the same order as that for ionic dyes of high aggregation tendency. MCT-TPDO displays no aggregation in water.

The values of K for PVS- and MCT-TPDO increase with an increase in the concentration of electrolyte. The aggregation promoted by the electrolyte is suppressed by addition of an organic solvent such as MP.

The interaction between TPDO molecules is attributed predominantly to enthalpic rather than entropic reasons in the case of the temperature dependence of aggregation.

PVS-TPDO which has been fixed to a cellulosic substrate shows aggregation tendency. The dimerization of PVS-TPDO is promoted by the immersion in water. The apparent value of K on dry cellulose is smaller by two orders of magnitude than that in water and is increased by swelling in water. TPDO reactive dyes on a nylon substrate show similar aggregation tendency to that on the cellulosic substrate. Thus, the existence of dimers for TPDO reactive dyes on cellulosic substrate was proved spectrophotometrically and the values of K were determined on cellulose as well as on water-swollen cellulose.

The aggregation character of the four TPDO dyes was similar in aqueous solution and on both cellulosic and nylon substrates, although it does not hold when reactive dyes with different structures are compared.

In practical dyeing, as sulfatoethylsulfonyl groups may be converted to vinylsulfonyl groups by alkali addition to the dyebath, the vinylsulfonyl form of the dye may display higher aggregation tendency. In this case, the aggregation behaviour of reactive dyes in the dyebath and on a cellulosic substrate to which they are fixed, may not be simply compared.

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