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The Stability and Reversibility of the Dye–Cellulose Bond for Vinylsulfonyl Reactive Dyeings

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ABSTRACT

The alkaline hydrolysis of eleven vinylsulfonyl (VS) reactive dyes (F-type) fixed on cellulose was examined at 50°C and pH 10·9. The reversibility of the dye–fiber bond was verified by the cylindrical-film-roll method, dyed and undyed cellulophane being used. The F-types were decomposed to yield the VS types, which were further hydrolyzed to yield the hydroxyethylsulfonyl types or reacted with cellulose to re-form the F-types. The F-types are composed of two kinds of species, presumed to arise from initial VS reaction with cellulose 6-OH or 2-OH, which showed fast and slow rates of bond scission, a bimodal hydrolytic behavior. CI Reactive Orange 7 and CI Reactive Yellow 17, which have a high reactivity with cellulose and a high initial rate of scission, were dyed at a similar ratio for both kinds of F-type and the other VS dyes at a relatively high ratio of the F-type, which undergoes slow hydrolysis.

NOTATION

A_i	Total concentration in the *i*th (initially dyed) layer ($i = 2n - 1$, $n \leq 6$) before scouring with boiling water after immersing in an aqueous alkaline solution (mol/kg)
B_i	Total concentration in the *i*th (initially undyed) layer ($i = 2n$, $n \leq 6$ and $i \geq 12$) before scouring and after immersing in an aqueous alkaline solution (mol/kg)
C_0	Initial concentration of F-type ($C_0 = C_{S0} + C_{F0}$) (mol/kg)
C_{F0}	Initial concentration of F-type undergoing fast hydrolysis (mol/kg)
C_{S0}	Initial concentration of F-type undergoing slow hydrolysis (mol/kg)

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C_t	Concentration of F-types after immersing in an aqueous alkaline solution for time t (mol/kg)
D_i	Concentration of unfixed (Hy + VS (+ their dimer)) species described by $A_i - F_i$ or $B_i - G_i$ on the ith layer (mol/kg)
F	Fixed species
F_i	Concentration of F-types on the ith (initially dyed) layer ($i = 2n - 1$, $n \leq 6$) (mol/kg)
G_i	Concentration of F-types on the ith (initially undyed) layer ($i = 2n$, $n \leq 6$ and $i \geq 12$) (mol/kg)
Hy	Hydroxyethylsulfonyl species
i	Number of layers from the surface of glass tubing
k_2	Apparent second-order rate constants of dimerization reaction between VS and Hy types[4] (dm^3/mol min)
k_C	Pseudo-first-order rate constant of reaction with cellulose[5] (min^{-1}) ($k_C = k_F + k_S$)
k_F	Pesudo-first-order rate constant of reaction with cellulose to form F-type undergoing fast hydrolysis (min^{-1})
k_{-F}	Pseudo-first-order rate constant of scission for F-type undergoing fast hydrolysis (min^{-1})
k_S	Pseudo-first-order rate constant of reaction with cellulose to form F-type undergoing slow hydrolysis (min^{-1})
k_{-S}	Pseudo-first-order rate constant of scission for F-type undergoing slow hydrolysis (min^{-1})
n	Positive integer (number of layers to describe the initially undyed ($2n$) and dyed ($2n - 1$) films)
VS	Vinylsulfonyl species

1 INTRODUCTION

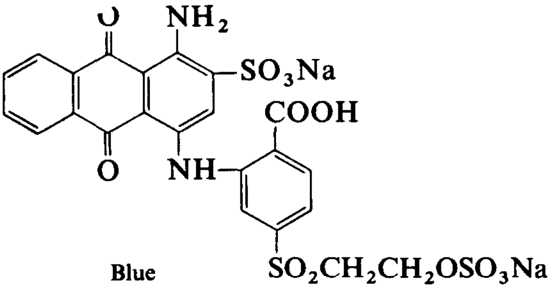
The reversibility of the reactive dye–cellulose bond has been suggested by Stamm in a reaction scheme for vinylsulfonyl (VS) dyes.[1] Senn and Zollinger[2] estimated the hydrolysis of the dye–cellulose bond for many kinds of reactive dyes over a wide range of pH conditions. Bond stability for CI Reactive Blue 19 was estimated only in VS dyes. The present authors[3,4] investigated the hydrolysis of VS dyes and estimated the rate constants of the reaction between the VS and the β-hydroxyethylsulfonyl (Hy) types. The rate constants of the forward and backward reaction of the dimerization varied widely with the VS dyes examined.

In the present study, bond scission of eleven VS reaction dyes fixed on a sheet of cellophane (F-types) is examined by immersing the dyed film in an aqueous alkaline solution. The migration and reaction of reactive dyes on cellulose immersed in the alkaline bath are also investigated by the cylindrical-film-roll method. It is confirmed that the VS types are formed from the reactive dyeings during the alkaline treatment and are either further hydrolyzed to yield the hydroxyethylsulfonyl types or reform the F-types accompanied by partial migration.

2 EXPERIMENTAL

2.1 Dyes used

VS dyes used were supplied by Mitsubishi Chemical Corporation and Sumitomo Chemical Co. Ltd. Their chemical structures are shown by the CI Constitution Number as shown in Table 1. The chemical structure of an anthraquinone dye, which has no CI Constitution Number, is shown below:



Blue

These dyes were used without further purification for dyeing. The molar-extinction coefficients were determined by the same method as previously used.[5] Chemicals used were of reagent grade.

2.2 Substrates

Cellophane sheets, 5·5 cm wide and 60 cm long, were scoured in boiling water to remove impurities and dyed by the alkali-shock method with sodium carbonate or by immersing the films in a dyebath containing sodium carbonate (20 g/dm^3) and sodium hydrogen carbonate (20 g/dm^3) (pH 9·6) at 50°C. The dyed films were scoured thoroughly in boiling water after dyeing.

Several sheets of this dyed cellophane (cut into 2-cm-long strips) were immersed in an aqueous sodium carbonate solution (0·10 mol/dm^3) at 50°C without stirring, since stirring was shown to have no effect on the rate of desorption. The external solution was sometimes renewed to avoid the readsorption of desorbed species. The optical densities of each film before and after immersion for different periods were measured at λ_{max} to obtain the degree of hydrolysis. After immersion, each film was thoroughly scoured in boiling water and dried prior to the optical measurement.

Two sheets of dyed and undyed cellophane were rolled on glass tubing.[5] On the rolled-film layer, a sheet of undyed film was further rolled. The length of rolled film was so adjusted that from the surface of a glass tube there were alternate dyed and undyed layers (a total of 12 layers) and six undyed layers. The F-types exist initially in the $(2n-1)$th layers ($n = 1$–6), whereas no coloured species were present in the $2n$th layers ($n = 1$–6) and above the 12th layers. The optical densities of each layer after the alkaline treatment were measured before and after being thoroughly scoured in boiling water. Those measured before the scouring correspond to A_i or B_i, and those after the scouring to F_i or G_i, respectively.

3 RESULTS AND DISCUSSION

3.1 Bond scission of fixed dyes on cellophane

The hydrolytic behavior of eleven VS dyes fixed on cellophane in an aqueous alkaline solution is shown in Fig. 1. It was confirmed that the initial concentration, C_0, of Yellow 17 and the dyeing method (pH 9·6 and 10·9) had no effect on the rate of desorption. We have also found,[6] by computer

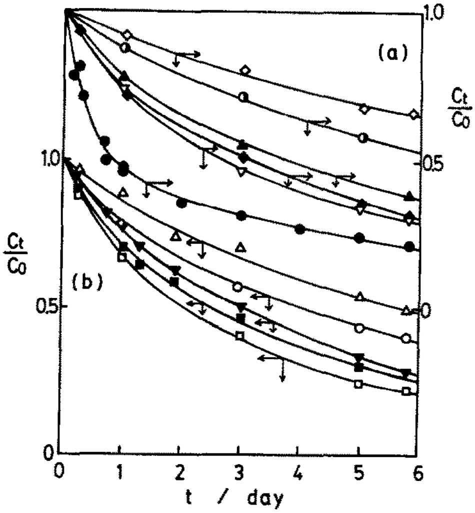


Fig. 1. Dye–cellulose bond scission of the F-types for VS dyes on cellophane immersed in an aqueous alkaline (0·10 mol/dm³ Na_2CO_3) solution at 50°C. (a) ▽ Yellow 13, ▲ Yellow 14, ● Yellow 17, ◑ Red 23; ◇ Violet 4, ◆ Violet 5; (b) □ Orange 7, ■ Orange 16, ○ Red 22, △ Blue 19, ▼ Blue.

simulation, that, under the present conditions (a sheet of dyed cellophane, pH 10·9, and 50°C), the rate of desorption is dependent only upon the rate constants of dye–fiber bond scission. The diffusion coefficient and affinity of the VS and Hy types, and the rate of reaction with cellulose of the VS types have little effect on the rate of desorption.[6] Thus, if straight-line plots of $\ln(C_t/C_0)$ versus t are obtained, the pseudo-first-order rate constant of scission can be calculated. Only Violet 4 gave a straight line, and Red 23 and Blue 19 gave almost a straight line, supporting the pseudo-first-order mechanism, while the other dyes gave a curve (Fig. 2(a)).

It was subsequently assumed that VS dyes that gave curved plots showed bimodal, fast and slow, hydrolytic behavior, and their rate constants are denoted by k_{-F} and k_{-S}, respectively. Since the fast hydrolysis proceeds preferentially, only the slow hydrolysis occurs after a sufficient time of alkaline treatment. By extrapolating the linear plots between $\ln(C_t/C_0)$ and t after long treatment to zero time, the values of initial concentration C_{S0} and k_{-S} for the slow hydrolysis were estimated.

Yellow 17, Red 22, Violet 5, and Blue showed the typical behavior, supporting the conclusion that this bimodal hydrolytic mechanism holds. The behavior for Yellow 17 and Violet 5 is shown in Fig. 2(a) as an example.

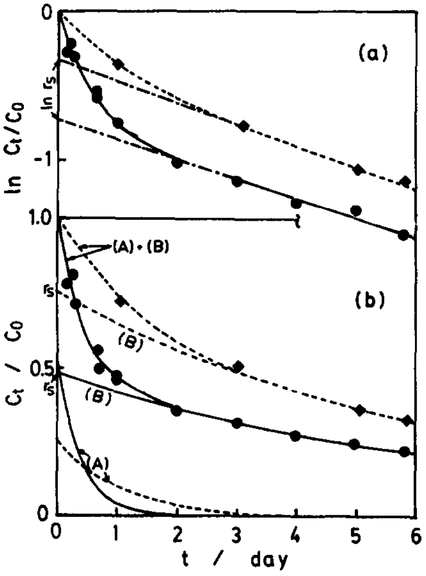


Fig. 2. (a) Relationship between $\ln(C_t/C_0)$ and time, and (b) the theoretical summed-up profile $\{C_t/C_0 = (C_{F0}/C_0)\exp(-k_{-F}t) + (C_{S0}/C_0)\exp(-k_{-S}t)\}$ of both the fast (A) and slow (B) pseudo-first-order hydrolyses described by the parameters shown in Table 1 for Violet 5 (◆) and Yellow 17 (●) in an aqueous sodium carbonate (0·10 mol/dm^3) solution at 50°C and pH 10·9. Theoretical curve: solid line for Yellow 17 and broken line for Violet 5.

Assuming that the fast and slow hydrolyses occur independently, and by using the above-mentioned values of C_{S0}, C_{F0}, and k_{-S} as the initial values, the best-fit values of C_{S0}, k_{-F}, and k_{-S} were determined by a least-mean-squares calculation so as to fit the sum of both the theoretical pseudo-first-order reaction profiles with the experimental hydrolytic profile, after being smoothed. Figure 2(b) shows that a superposition of two kinds of the pseudo-first-order hydrolysis agrees well with the experimental plots for two dyes. Although, in the cases of Yellow 13, Yellow 14, Orange 7, and Orange 16, the convergence domain for the fittest values was wide, owing to the smaller values of k_{-F}/k_{-S} and the larger values of C_{F0}/C_{S0} compared with the other dyes, their values were also estimated by the same method. The relative concentration of F-types undergoing fast and slow hydrolyses and the values of their rates of scission are shown in Table 1.

The relative initial concentrations, C_{S0}/C_0, for the F-types undergoing slow hydrolysis were, in general, dominant, but those for Orange 7 and Yellow 17, which underwent the fastest initial hydrolysis, were comparable with those for the F-type undergoing fast hydrolysis.

Bimodal hydrolytic behavior is supposed to correlate with the position of hydroxyl groups, 2-OH and 6-OH, in cellulose, with which VS dyes react. Stamm[7] reported that Blue 19 reacted mainly with 2-OH, but Bhagwanth *et al.*[8] reported that a model VS compound reacted mainly with 6-OH. Since the present study implies that the particular hydroxyl group of cellulose with which the VS dyes react varies from dye to dye, their results may not be contradictory to each other. The F-types undergoing slow hydrolysis are supposed to correlate with the reactive dye fixed species at the 2-OH residue, if Stamm's result is taken into consideration.[7]

From the values of the pseudo-first-order rate constant, k_C,[5] with cellulose and the values of k_{-F}, k_{-S}, C_{F0}, and C_{S0} determined in the present paper, the values of various kinetic parameters for VS dyes were estimated as shown in Table 1. When the pseudo-first-order rate constants of reaction to yield the F-types undergoing fast and slow hydrolyses are denoted by k_F and k_S, C_{F0}/C_0 and C_{S0}/C_0 may be equal to $k_F/(k_F+k_S)$ and $k_S/(k_F+k_S)$, respectively. The values of k_C for VS dyes may be equal to those of $k_F + k_S$. It is worth noting that k_F and k_S are the products of the second-order rate constants of reaction and the concentration of the corresponding cellulosate ion. Orange 7 and Yellow 17, which have high reactivity with cellulose[5] and a high initial rate of scission, may have similar values of k_F and k_S, whereas the other VS dyes have a larger value of k_S than of k_F. In general, the F-types undergoing slow hydrolysis have very small values of k_{-S}/k_S and a high bond stability, whereas those undergoing fast hydrolysis have a larger value of k_{-F}/k_F and a high reversibility, as mentioned below (cf. Section 4.2), than of k_{-S}/k_S. Although the formation of F-types undergoing fast hydrolysis is

TABLE 1

VS Dyes Used, Initial Concentration, C_0, Relative Concentrations, C_{F0}/C_0 and C_{S0}/C_0, for F-Types Undergoing Fast and Slow Hydrolyses, and their Rates of Formation, k_C,* k_F, and k_S, and of Bond Scission, k_{-F} and k_{-S}, at pH 10·9 and 50°C

CI Reactive Dye	*CI Constitution Number*	$C_0 \times 10^2$ (*mol/kg*)	C_{F0}/C_0	$k_{-F} \times 10^4$ (*min*$^{-1}$)	C_{S0}/C_0	$k_{-S} \times 10^4$ (*min*$^{-1}$)	$k_C \times 10^2$ (*min*$^{-1}$)	$k_F \times 10^2$ (*min*$^{-1}$)	$k_S \times 10^2$ (*min*$^{-1}$)	$k_{-F}/k_F \times 10^2$	$k_{-S}/k_S \times 10^2$
Yellow 13	18 990	0·317	0·35	4·86	0·65	0·97	4·0	1·4	2·6	3·5	0·37
Yellow 14	19 036	0·158	0·35	3·96	0·65	0·69	5·0	1·75	3·25	2·3	0·21
Yellow 17	18 852	3·49‡	0·52	16·7	0·48	0·97	10·3	5·36	4·94	3·1	0·20
Orange 7	17 756	2·09	0·40	6·25	0·60	1·25	17·8	7·12	10·7	0·9	0·12
Orange 16	17 757	1·63	0·35	5·90	0·65	1·11	5·8	2·03	3·77	2·9	0·29
Red 22	14 824	2·43	0·20	6·25	0·80	0·83	9·0	1·8	7·2	3·5	0·12
Red 23	16 202	0·937	0·05	8·68	0·95	0·69	4·8	0·24	4·56	36·2	0·15
Violet 4	18 096	1·07	0	—	1·0	0·56	2·3	—	2·3	—	0·24
Violet 5	18 097	1·16	0·25	7·29	0·75	1·04	7·0	1·75	5·25	4·2	0·20
Blue 19	61 200	3·31	0·05	6·25	0·95	0·83	8·0	0·40	7·6	15·6	0·11
Blue	—	2·73	0·15	5·90	0·85	1·39	—§	—	—	—	—

* Values of k_C at pH 10·9 and 50 C estimated from the values obtained previously.[5]

‡ Sample of $C_0 = 5{\cdot}90 \times 10^{-3}$ mol/kg gave the same results.

§ Not determined.

slow, the F-types for Red 23 and Blue 19 have similar rates of bond scission to those for the other VS dyes.

On the whole, VS dyes with low affinity to cellulose gave smaller values of C_{F0}/C_0, although high values of C_{F0}/C_0 were not given by all the dyes with high affinity.

The problem of the reaction site of cellulose, however, remains to be solved.

3.2 Reversibility of the dye–cellulose bound

The VS and Hy types adsorbed on cellophane for six dyes shown in Table 2 were first confirmed to be completely removed by boiling the adsorbed film in water for 20 min. The fixed species could not practically be removed by immersing the dyed film in boiling water under neutral conditions.

The dye distribution in dyed cellophane and the stability of the dye–fiber bond in an alkaline treatment were examined by the cylindrical-film-roll method, dyed and undyed cellophane being used. The distribution of various species for Yellow 17 after an alkaline treatment at 50°C for 24 h is shown in Fig. 3 as an example.

Although the degree of migration G_i/C_0 varied with the dyes, the F-types for all the VS dyes migrated into the undyed layers to re-form the F-types in the alkaline treatment, as shown by the values of G_i for F-types in the initially undyed layers (Fig. 3 and Table 2). This fact shows that, under the alkaline conditions, the F-types of all the VS reactive dyeings revert to the VS types, which during migration react with water to lose reactivity or again with cellulose to re-form the F-types, a slow migration of the F-type being accompanied by partial hydrolysis. In some cases, the dimer between the VS and Hy types may be formed in the processes.

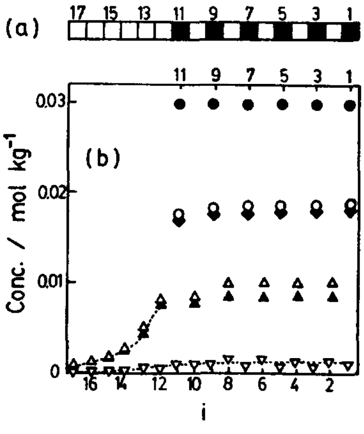


Fig. 3. (a) Initial state (■ F-type, □ undyed) of film layers and (b) distribution of various species (● C_0, ○ A_i, ◆ F_i, △ B_i, ▲ G_i, ▽ D_i) of Yellow 17 in initially dyed and undyed cellophane layers after being dipped in an aqueous alkaline (0·05 mol/dm^3 Na_2CO_3) solution at 50°C and pH 10·7 for 24 h.

TABLE 2
Mean Distribution of Various Species for VS Dyes after an Alkaline Treatment (0·05 mol/dm^3 Na_2CO_3) at 50°C and pH 10·7 for 24 h ($1 \leq i \leq 7$) and Analyses of Reversibility of Dye–Cellulose Bond

CI Reactive Dye	*Yellow 17*	*Orange 7*	*Orange 16*	*Red 22*	*Blue 19*	*Blue*
$C_0 \times 10^2$ (mol/kg)	2·94	4·73	3·82	4·19	2·33	5·65
$A_{2n-1} \times 10^2$ (mol/kg)	1·89	4·03	3·12	3·77	2·18	4·92
$F_{2n-1} \times 10^2$ (mol/kg)	1·81	3·82	3·10	3·49	2·17	4·79
$B_{2n} \times 10^2$ (mol/kg)	1·02	0·668	0·687	0·379	0·144	0·692
$G_{2n} \times 10^2$ (mol/kg)	0·877	0·657	0·682	0·355	0·109	0·633
F_i/C_0	0·616	0·808	0·810	0·833	0·931	0·848
$(F_i - G_{i+1})/C_0$	0·317	0·669	0·638	0·748	0·885	0·734
G_i/B_i	0·860	0·984	0·993	0·937	0·757	0·915

3.3 Dye distribution after alkaline treatment

When the relationship between $(A_i - F_i)$ or $(B_i - G_i)$ and i ($1 \leq i \leq 17$) is plotted, the unfixed (Hy + VS (+their dimer)) species D_i is evenly distributed, as shown in Fig. 3. Within the tenth layer, the VS species reverted from the initially dyed layers and seemed to migrate to the next layers, indicating no reduction of total dyes. The fact that $C_0 - A_i$ equals B_{i+1} shows that the reverted VS species diffuses evenly into the adjacent initially undyed layers.

The mean concentrations of various species within the tenth layer for six VS dyes after an alkaline treatment are summarized in Table 2 ($1 \leq i \leq 7$). The apparent alkaline stability for six VS dyes estimated by the mean value of F_i/C_0 ($1 \leq i \leq 7$) followed in the order shown in Table 2:

$$\text{Blue 19} > \text{Blue} > \text{Red 22} > \text{Orange 16} = \text{Orange 7} > \text{Yellow 17} \qquad (1)$$

The apparent stability shown by the order (1) is closely similar to the stability examined above (cf. Section 3.1).

The apparent degree of scission estimated by $1 - (F_i - G_{i+1})/C_0$ ($1 \leq i \leq 7$) was in the following order:

$$\text{Yellow 17} > \text{Orange 16} > \text{Orange 7} > \text{Blue} > \text{Red 22} > \text{Blue 19} \qquad (2)$$

This order is almost the same as the initial rate of scission examined above (cf. Section 4.1).

The fixation ratios G_i/B_i in the initially undyed layers for Yellow 17 and

Blue 19 were a little smaller than those for the other dyes, implying an effect of dimerization of Yellow 17 and Blue 19, which have large values of k_2 compared with the other VS dyes.[4] The VS types may react with the Hy type existing evenly in each layer to form the dimer, which suppresses the re-formation of the F-type. Since the value of k_2 for Orange 16 is much smaller than that for Yellow 17 and Blue 19 although it forms the dimer,[4] no effect is observed in the case of Orange 16.

On immersion in an aqueous alkaline solution, VS dyes fixed on cellulose not only show reversibility but also the effect of dimerization if they have large values of k_2.

4 SUMMARY

VS dyes fixed on cellulose show bimodal (slow and fast) hydrolytic behavior on receiving an alkaline treatment. The bimodal character may correlate with the position of the particular hydroxyl dye site in cellulose. The rate of faster scission for the F-type of half of the VS dyes examined is five times as great as that of those undergoing slow hydrolysis. The rate of scission for F-types of the other VS dyes undergoing fast hydrolysis is from six to twenty times as great as when they are undergoing slow hydrolysis. The rates of slower hydrolysis are nearly the same for all VS dyes examined. The relative ratio of production for two kinds of F-type varies with the dyes. In general, VS dyes with low affinity to cellulose showed low values of C_{F0}/C_0.

Under alkaline conditions, the F-types are hydrolyzed to yield the VS type, which migrates in the substrate and reacts with cellulose to reproduce the F-type or with water to yield the Hy type, which diffuses in cellulose and is described into the external solution.

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