

Diffusion of Dye Mixtures in Nylon 6. Binary Mixtures of Disperse Dyes

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Synopsis

The diffusion of binary dye mixtures of markedly different chemical constitutions (4-nitro-4'-aminoazobenzene and 1-amino-4-hydroxyanthraquinone) and of similar ones (1-amino-4-hydroxyanthraquinone and 1,4-dihydroxyanthraquinone) into nylon 6 film was examined. Apparent diffusion coefficients of dyes in the mixture within a single dyeing were determined by the film roll method at 60°, 70°, 80°, and 90°C. Diffusion coefficients of individual dyes used in a mixture of chemically dissimilar dyes are found to change little in comparison with single dyeings, while diffusion coefficients of dyes of similar structures are decreased appreciably. It is suggested that the latter effect is due to the interaction between two dyes in the fiber substrate.

INTRODUCTION

Generally, the dyeing mechanism of nylon with disperse dyes can be regarded as comparatively simple in comparison to dyeing systems of ionic character. However, mixture dyeing of the same fiber/dye system is still subject to research. The first attempts to describe the mutual interactions of dyes on dyeing hydrophobic substrates with binary mixtures of disperse dyes were made by Vickerstaff and Waters¹ and Bird and Rhyner.² Further contributions were made, in particular, by Schuler and Remington,³ Johnson et al.,⁴ and Hoffmann et al.⁵ These equilibrium sorption studies revealed that the saturation values in hydrophobic substrates of binary dye mixtures of certain disperse dyes are additive, but the dyes of binary mixtures of similar chemical constitution are sorbed to a smaller extent than when they are applied individually.

However, little work has been carried out on the diffusion of mixtures of disperse dyes in hydrophobic substrates. In this work, an investigation has been done to elucidate the diffusion mechanism of mixtures of disperse dyes in nylon. Dye combinations of different, and of similar, chemical constitution were used to determine the diffusion coefficients. Single dyeing of these dyes as well as mixture dyeing were carried out by the film roll method.⁶

EXPERIMENTAL

The dyes used were 4-nitro-4'-aminoazobenzene (I), 1-amino-4-hydroxyanthraquinone (II), and 1,4-dihydroxyanthraquinone (III). Dye I was prepared

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by coupling of diazotized *p*-nitroaniline with sodium *N*-methylaniline- ω -sulfonate which was synthesized from freshly distilled aniline and recrystallized several times from ethanol to give a product having a sharp melting point, 211°C (uncorrected). Elemental analysis of this product ($C_{12}H_{10}N_4O_2$) gave C, 59.16%; N, 23.07%; H, 3.93% (calcd. C, 59.50%; N, 23.14%; H, 4.13%). Extra pure 1-amino-4-dihydroxyanthraquinone and the same grade of 1,4-dihydroxyanthraquinone were recrystallized three times from ethanol. The melting points of dye II and dye III were 215° and 201°C, respectively.

Biaxially drawn nylon 6 film (Unitika Ltd.) 15 μ thick and having 4.09×10^{-5} eq. amino endgroup/g was used throughout this work. In each experiment, the film roll was prepared as reported earlier.⁷ Before dyeing, the film roll was immersed in deionized water of the same temperature of dyeing and then transferred to a previously prepared infinite dyebath.⁸ A piece of film of about 3 cm \times 4 cm was also immersed in the bath to determine the surface concentration.

Diffusion experiments were carried out in a 500-ml diffusion vessel at 60°, 70°, 80°, and 90° \pm 0.1°C. Each dyebath was prepared in less than the aqueous solubility of the dye. Infinite dyebath condition was maintained during dyeing by transferring the film roll to another freshly prepared dyebath of the same composition. After dyeing, the visible absorption spectrum of each layer of the film roll was obtained by means of a Shimadzu Multiconvertible Double-40 spectrophotometer. The concentration of each dye in mixture dyeing was calculated from the absorbance values at two suitable wavelengths.⁹ A film roll used in the experiment may well be considered a semiinfinite medium in the lateral direction of the roll; thus, if the surface dye concentration is constant during the experiment, the diffusion coefficient can be calculated from the concentration profile.⁶

The absorption spectra of dye solution were determined with the aid of a 100-mm-long cell which was thermostated (\pm 0.1°C).

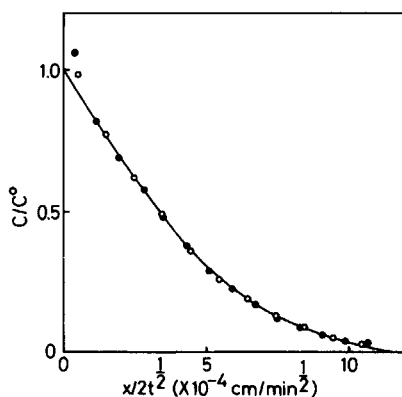


Fig. 1. Concentration profiles for dye II at 90°C (dyebath concentration = 4.7×10^{-5} mole/kg solution): (O) 60 min; (●) 90 min; C , dye concentration of in each layer at time t ; C^0 , dye concentration at the surface of the film roll; x , penetration distance.

RESULTS AND DISCUSSION

Because of low aqueous solubilities of disperse dyes, diffusion coefficients were determined from the saturated solution in single dyeing, and the solutions of binary dye mixture were prepared by mixing each individual solution. Thus, the concentration of diffusant in solution was not fixed in each experiment. However, this should not be an obstacle in interpreting the results, since the concentration dependence of the diffusion coefficient was not observed in this system¹⁰ in the concentration range investigated. The dyeing times were chosen so as to allow diffusion of dye not further than the third layer counted from the innermost layer of a film roll. Typical concentration profiles obtained from single dyeing are shown in Figure 1, as C/C_0 against $x/2t^{1/2}$, where C is the concentration of dye at distance x , C_0 is surface concentration, and t is time. Here, it is clearly shown that the diffusion coefficient is independent of the concentration of the dye in the substrate. Dye distributions of the mixture of dyes I and II and dyes II and III (molar ratio of 1:1) at 70°C are shown in Figures 2 and 3, which are typical examples. Similar concentration profiles were obtained in other dyeing conditions. From these profiles, diffusion coefficients were calculated as shown in Table I.

As seen in Table I, the diffusion coefficients of dyes I and II binary mixture are almost unaltered ($\pm 5\%$ for average value), in comparison to single dyeing. On the other hand, there is a general trend that the diffusion coefficients of dyes II and III in binary mixtures become smaller than that of single dyeing.

It might generally be thought that the lowering of diffusion coefficients in mixture dyeing is due to one or more of the following causes: (1) interaction between two dyes in the aqueous phase, (2) interaction between two dyes in the polymer phase, and (3) competitive interaction of two dyes with the polymer matrix.

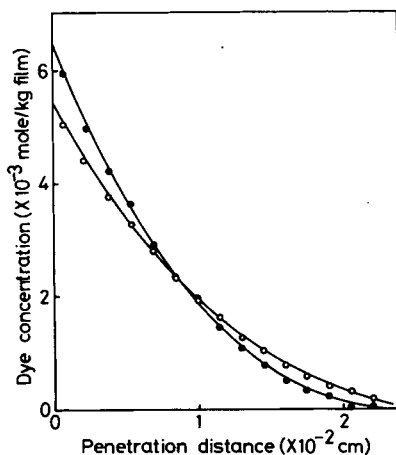


Fig. 2. Concentration profiles in a mixture of dyes I and II at 70°C, 480 min (molar mixture ratio = 1:1; dyebath concentration = 7.0×10^{-6} mole/kg solution, respectively): (O) dye I; (●) dye II.

TABLE I
Diffusion Coefficients of Dyes in Nylon 6 at Various Temperatures^a

Temp., °C	Single dye			Mixture (1:1) ^b			Mixture (1:2)			Mixture (2:1)			Mixture (1:1)			Mixture (1:2)			Mixture (2:1)		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
	5.3 ₃	4.4 ₉	3.7 ₇	6.0 ₁	4.4 ₇	4.4 ₇	5.3 ₈	4.0 ₈	5.3 ₇	3.4 ₉	3.4 ₉	3.4 ₉	3.6 ₂	3.6 ₂	3.4 ₃	3.5 ₃	3.5 ₃	3.1 ₆	3.6 ₃	3.6 ₃	3.6 ₃
70	13.1	9.7 ₇	6.9 ₉	13.0	9.8 ₁	9.8 ₁	13.0	10.2	12.6	8.9 ₁	8.9 ₁	7.2 ₈	7.2 ₈	6.8 ₉	8.2 ₀	8.2 ₀	6.4 ₆	6.6 ₄	6.6 ₄	6.6 ₄	6.6 ₄
80	33.3	23.4	19.4	29.4	24.8	24.8	30.4	23.8	32.1	25.8	25.8	20.9	20.9	20.5	16.8	16.8	17.8	17.8	17.8	21.0	16.6
90	66.7	47.3	43.8	62.6	53.9	53.9	66.0	52.8	70.0	54.2	54.2	40.7	40.7	36.7	40.7	40.7	43.9	43.9	43.9	45.8	38.6

^a Units of D are $\times 10^{-8}$ cm²/min.

^b Molar ratio.

Johnson et al.⁴ found that mixtures selected from dyes of dissimilar structure show no interaction. Each of them is sorbed from the mixture to the same extent as that of corresponding single dyeing. These mixtures give an eutectic point in their melting point diagrams, whereas mixtures of interacting (similar structure) dyes show no such point. They assumed that an interaction similar to what occurs in the solid state can also take place in the fiber. On the contrary, Hoffmann et al.⁵ gave an alternative explanation for this phenomenon, namely, that the ability to form mixed crystals only affect the behavior in aqueous dispersion, since these dyes are always monomolecularly dispersed in the fiber phase.

To investigate the interaction of dyes in the dyebath, the absorption spectra of dye solutions were measured at 25°C and 60°C. It can be seen from Figure 4 (25°C) that the observed spectrum of the mixture of dyes I and II shows some sign of interaction as well as the mixture of II and III. In the latter case, the deviation from additivity is more obvious. Similar results were obtained at 60°C. The effective dye concentration for diffusion into polyamide will decrease by the results of the interaction between dyes in the dye bath. The lowering of surface concentration on polyamide substrate follows. But the diffusion coefficient does not change because the coefficient is independent of the concentration of dye in the wide range of concentration in the case of disperse dye-polyamide system. Accordingly, it is concluded that the cause for the decrease of, the diffusion coefficient in binary mixtures should be attributed to (2) or (3) mentioned above.

In order to estimate the effect of interaction in the polymer phase, the cross-term diffusion coefficients were calculated.

The two diffusional flows in the dyeing of binary mixture, J_1 and J_2 , are written as follows¹¹:

$$J_1 = -D_{11} \frac{\partial C_1}{\partial x} - D_{12} \frac{\partial C_2}{\partial x} \quad (1)$$

$$J_2 = -D_{21} \frac{\partial C_1}{\partial x} - D_{22} \frac{\partial C_2}{\partial x} \quad (2)$$

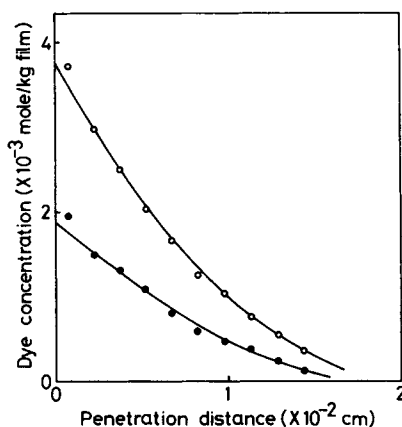


Fig. 3. Concentration profiles in a mixture of dyes II and III at 70°C, 480 min (molar mixture ratio = 1:1; dyebath concentration = 3.8×10^{-6} mole/kg solution, respectively): (O) dye II; (●) dye III.

where dye concentrations C_1 and C_2 are functions of distance x and time t , D_{11} and D_{22} are the main diffusion coefficients, and D_{12} and D_{21} are the cross-term diffusion coefficients. Let D_1' and D_2' be apparent diffusion coefficients of dyes 1 and 2 in the mixture dyeing, and eqs. (1) and (2) become

$$J_1 = -\left(D_{11} + D_{12}\frac{\partial C_2}{\partial C_1}\right)\frac{\partial C_1}{\partial x} = -D_1'\frac{\partial C_1}{\partial x} \quad (3)$$

$$J_2 = -\left(D_{21}\frac{\partial C_1}{\partial C_2} + D_{22}\right)\frac{\partial C_2}{\partial x} = -D_2'\frac{\partial C_2}{\partial x} \quad (4)$$

Then

$$D_1' = D_{11} + (D_{12}/k) \quad (5)$$

$$D_2' = D_{21}k + D_{22} \quad (6)$$

where

$$k = \partial C_1 / \partial C_2 \quad (7)$$

Let us assume¹¹ that

$$D_{11} = D_1, \quad D_{22} = D_2 \quad (8)$$

where D_1 and D_2 refer to the diffusion coefficients when diffusing alone. D_1 , D_2 , D_1' , D_2' can be determined experimentally. $\partial C_1 / \partial C_2$ is also determined by plotting the values of C_1 and C_2 from the concentration profiles in mixture diffusion, and the results are shown in Figure 5 as an example. From this result, one can assume the value of $\partial C_1 / \partial C_2$ is constant. Thus, D_{12} and D_{21} have been calculated, and the results at 60°C are given in Table II.

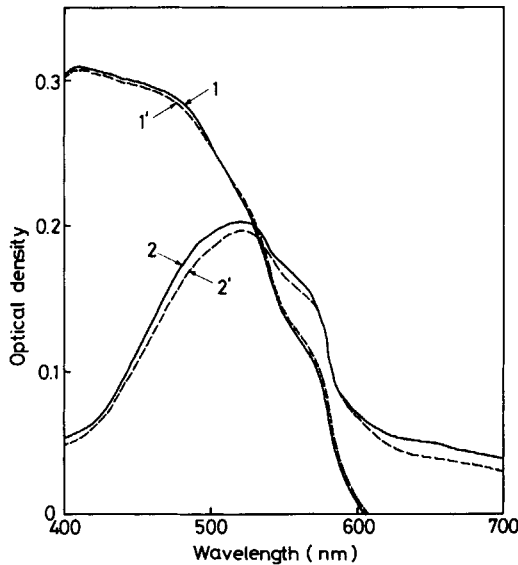


Fig. 4. Absorption spectra of dye mixtures at 25°C: (1) calculated curve based on additivity, dyes I and II; (1') observed spectrum of dye mixture I and II; (2) calculated, dye II and III; (2') observed, dyes II and III. Concentration of each dye is 1.50×10^{-6} mole/l.; cell thickness = 10 mm.

TABLE II
Cross-Term Diffusion Coefficients at 60°C^a

Molar mixture ratio	$D_{I,II}$	$D_{II,I}$	$D_{II,III}$	$D_{III,II}$
2:1	0.05	-0.74	-2.53	-0.04
1:1	0.50	-0.03	-1.76	-0.17
1:2	0.02	-1.05	-1.07	-0.55

^a Units of D are $\times 10^{-8}$ cm²/min.

As the values of $D_{I,II}$ are slightly plus or nearly equal to zero while $D_{II,I}$, $D_{II,III}$ and $D_{III,II}$ are minus, it is considered that the diffusion of dye I is only slightly accelerated by the presence of dye II. The sign of the cross-term diffusion coefficient indicates the retardation of diffusion of dye II in the presence of dye III, and vice versa. Though it is difficult to conclude quantitatively from this result, it may be said at least that the effect of dye I on the diffusion of dye II is smaller than that of dye III on the diffusion of dye II in each respective mixture. In other words, a dye of similar structure has more interaction compared with the case of dissimilar structure.

It is generally accepted that the dyeing of polyamide with disperse dyes is governed by a solution mechanism. Of course, in a molecular sense, a "site" in polyamide for disperse dye can be assumed even in a solution mechanism. The amount of sites are very large, in that case resulting in a Nernst type of sorption isotherm and, consequently, in independence of the diffusion coefficient on the dye concentration. Even if the interaction of two individual dyes having similar chemical constitution for the same site exists, the amount of the site is still sufficiently large to occupy freely without competition. The situation was proved by the fact that the individual diffusion coefficient in binary mixtures is not dependent on the concentration in the dyebath conditions examined in this work. Accordingly, the decrease in the diffusion coefficient should be attributed to the interaction of dye in the polymer matrix.

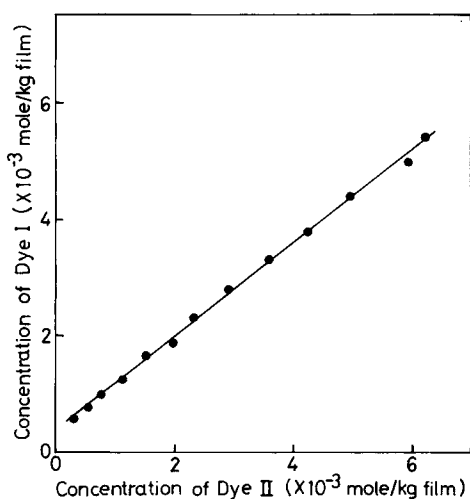


Fig. 5. Ratio of dye I to dye II in polymer in mixture dyeing. Data are the same as in Fig. 2.

TABLE III
Partition Coefficients of Dye II

Temp., °C	K_{II} Single ($\times 10^2$) ^a	K_{II} Mixture with dye III ($\times 10^2$) ^a			
		2:1	1:1	1:2	1:3
60	5.90	7.23	7.51	7.88	—
70	4.61	4.25	4.73	5.72	—
80	2.79	3.32	3.55	3.33	—
90	1.89	1.92	2.07	2.02	1.93

^a Calculated from the values of surface concentration C_o and dyebath concentration C_g . C_o corresponds to the equilibrium sorption under the infinite dyebath condition in this work.

^b Molar ratio (dye II:dye III).

TABLE IV
Diffusion Coefficients of Dye II and Orange II in Mixture Dyeing^a

Temp., °C	Orange II alone	Mixture		Mixture		Mixture	
		II (1:1)	Orange (1:1)	II (1:2)	Orange (1:2)	II (2:1)	Orange (2:1)
60	1.5 ₄	3.9 ₇	1.6 ₁	4.0 ₅	1.5 ₆	4.3 ₇	1.5 ₁
70	3.8 ₀	9.6 ₈	3.9 ₈	9.1 ₂	3.9 ₀	9.2 ₇	3.4 ₈
80	8.2 ₁	22 ₉	8.8 ₇	21 ₄	7.6 ₅	22 ₂	8.4 ₅
90	18 ₁	48 ₆	18 ₈	51 ₉	19 ₃	50 ₇	19 ₆

^a Units of D are $\times 10^{-8}$ cm²/min.

When we assume the diffusion mechanism of disperse dye in polyamide as that of a "porous structure" model, the total amount of dye i in polymer, C_i , should be written as follows:

$$C_i = C_i^f + C_i^b = C_i^f (1 + K_i) \quad (9)$$

where C_i^f refers to the concentration of free dye in water in polymer, C_i^b is bound dye with polymer matrix, and K_i is the partition coefficient between polymer matrix and water in polymer phase. Assuming that (1) sorption equilibrium is established instantaneously in every local part of polymer phase, and (2) the driving force of diffusion is only the concentration gradient of free dye in polymer, the apparent main diffusion coefficient, D_{ii} can be written as $D_{ii}^0 [1/(1 + K_i)]$, where D_{ii}^0 is the main diffusion coefficient for free mobile dye. In this context, the greater the K_i , the smaller the D_{ii} . In Table III one can find a greater value of K_{II} in mixture dyeing than for single dyeing.

The diffusion of mixtures of dye II and acid dye, which obviously differs in dyeing mechanism, was examined. In Table IV diffusion coefficients of dye II and Orange II are given. No change in diffusion coefficients of dye II is observed in mixture dyeing or single dyeing. This is supported by the absorption spectra of mixture solution of these dyes in that there is no sign of interaction between these two dyes. It is generally accepted that like dis-

solves like, i.e., dyes that have similar chemical constitutions interact with each other and dyes of dissimilar chemical constitutions have little interaction. This may hold in polymer phase.

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