Studies on Mixture Dyeing. I. The Kinetics of the Mixture of Benzopurpurine 4B and Sky Blue 6B

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In practical dyeing, dye mixtures are usually used to produce a desirable shade. Moreover, some commercial dyes are deliberate mixtures in order to provide certain specific properties and shades. This implies that to study dyeing is practically the same as to study mixture dyeing. However, little has been done in the quantitative study of such mixture dyeing. Neale and Stringfellow[1] and recently Horiki et al.[2,3] have investigated the equiliburium adsorption of binary direct dye mixtures, but the diffusion of dye mixtures has been little studied. Recently, however, many studies of diffusion in multi-component systems have been made from the view point of the thermodynamics of irreversible processes[4]. Uedaira[5] and Tsuda[6] applied this theory to the mixture dyeing process.

For this paper, the kinetics of the single dyeing of Benzopurpurine 4B (C. I. 23500) and of Sky Blue 6B (C. I. 24410) has been investigated in detail in order to study quantitatively their behavior in mixture dyeing. Then the kinetics of mixture dyeing has been studied theoretically on the basis of the information about the single dyeing.

Experimental

Purified dyes were used throughout. They were prepared from commercial dyes (Diacotton Benzopurpurine 4B (MCI) and Diacotton Sky Blue 6B (MCI)) by the method of Robinson and Mills[7]. The high purity of these samples was checked by titanometry and also by the ashing method. The absence of colored impurities was confirmed by paper chromatography.

A cellophane sheet, made by Tokyo Cellophane Co., Ltd., was used as the dyeing substrate. It was cut into pieces 6 cm. wide and 55 cm. long, which pieces were then scoured by distilled water and layered round on a glass tube. This cylindrical cellophane-film roll[8] was dyed under certain conditions. After dyeing, the film roll was rinsed in a dilute sodium chloride solution for a short time. Then the dyed cellophane was unrolled and dried. The dried sample was cut, layer by layer, for colorimetry by a Hitachi EPB-V type spectrophotometer, or the dyes adsorbed by each layer were stripped with 25% aqueous pyridine and the dye content of the solution was measured by the spectrophotometer. The mean thickness of each swollen cellophane sheet was 4.66×10^{-3} cm.

In single dyeing, the concentration of dye in the dye bath was 1.0, 2.5, 5.0, or 10.0×10^{-5} mol./l., while that of sodium chloride was 0.01, 0.02, 0.03, or 0.04 mol./l. In mixture dyeing, the experimental conditions were as shown in Tables IV and V. The dyeing time was 3000 min. (90°C); 4500 min. (85°C); 6000 min. (80°C) or 7500 min. (75°C).

Theoretical

The cylindrical cellophane roll[8] may well be considered a semi-infinite media in the direction of the center of the roll. The surface dye concentration of rolled cellophane is maintained constant throughout the whole period of dyeing by means of the infinite dye bath condition.

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1) S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Colourists*, 59, 243 (1943).
2) Y. Horiki, Y. Tanizaki and N. Ando, This Bulletin, 33, 163 (1960).
3) Y. Horiki, ibid., 33, 974 (1960).
4) D. G. Miller, *Chem. Revs.*, **60**, 15 (1960).
5) H. Uedaira, *J. Soc. Textile Cellulose Ind. Japan* (*Sen-i Gakkaishi*), **14**, 967 (1958).
6) K. Tsuda, the 13th Annual Meeting of the Chemical Society of Japan, 1959.
7) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.*, **A131**, 576 (1931).
8) M. Sekido, *Annual Report of the 120th Committee of Science Promoting Society of Japan*, **5**, 113 (1953); **6**, 75 (1954); **7**, 56 (1955); **8**, 39 (1956).

Single Dyeing.—Assuming that the diffusion coefficient of dye through the dyeing substrate, D (cm^2/min.), is constant at a given temperature and concentration of dye and electrolyte in the dye bath, the diffusion equation is

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C (mol./cm^3 s. c.*) denotes the concentration of dye in the substrate, t (min.), the time, and x (cm.), the distance measured from the surface to the center. The solution of Eq. 1 for this system is

$$\frac{C}{C_0}=\mathrm{erfc}\frac{x}{2\sqrt{Dt}} \qquad (2)$$

where

$$\mathrm{erfc}\, x=\frac{2}{\sqrt{\pi}}\int_x^{\infty} e^{-\eta^2}d\eta \qquad (3)$$

and C_0 is the surface concentration of dye.

The calculation of the diffusion coefficient and of the surface dye concentration can be made by the method of Sekido and Matsui[9].

Mixture Dyeing.—The diffusion of a mixture of dyes has recently been studied by Uedaira[5] and by Tsuda[6]. Assuming for the diffusion coefficient the same conditions as those in the case of single dyeing, the diffusion equations of binary mixture dyeing[5,10] are

$$\frac{\partial C_1}{\partial t}=D_{11}\frac{\partial^2 C_1}{\partial x}+D_{12}\frac{\partial^2 C_2}{\partial x^2} \qquad (4)$$

$$\frac{\partial C_2}{\partial t}=D_{21}\frac{\partial^2 C_1}{\partial x^2}+D_{22}\frac{\partial^2 C_2}{\partial x^2} \qquad (5)$$

where C_1 and C_2 are the concentrations of dyes 1 and 2 respectively, D_{11} and D_{22} are the main diffusion coefficients, and D_{12} and D_{21} are the cross-term diffusion coefficients.

These equations may be solved by the method of Fujita and Gosting[11], as was done by Uedaira[5]. The initial and boundary conditions are

$$C_1=C_2=0, \qquad x>0, \qquad t=0 \qquad (6)$$

$$C_1=C_1^{\circ}, \qquad C_2=C_2^{\circ}, \qquad x=0, \qquad t>0 \qquad (7)$$

where C_1° and C_2° are the surface concentrations of dyes 1 and 2 respectively.

Therefore, the solutions of these equations are

$$\frac{C_1}{C_1^{\circ}}=K_1^{+}\,\mathrm{erfc}\frac{\sqrt{\sigma_+}}{2\sqrt{t}}x+K_1^{-}\,\mathrm{erfc}\frac{\sqrt{\sigma_-}}{2\sqrt{t}}x \qquad (8)$$

$$\frac{C_2}{C_2^{\circ}}=K_2^{+}\,\mathrm{erfc}\frac{\sqrt{\sigma_+}}{2\sqrt{t}}x+K_2^{-}\,\mathrm{erfc}\frac{\sqrt{\sigma_-}}{2\sqrt{t}}x \qquad (9)$$

where

$$K_1^{+}=\frac{(D_{22}-D_{11})+\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}-2D_{12}C_2^{\circ}/C_1^{\circ}}{2\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}} \qquad (10)$$

$$-K_1^{-}=\frac{(D_{22}-D_{11})-\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}-2D_{12}C_2^{\circ}/C_1^{\circ}}{2\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}} \qquad (11)$$

$$K_2^{+}=\frac{(D_{11}-D_{22})+\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}-2D_{21}C_1^{\circ}/C_2^{\circ}}{2\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}} \qquad (12)$$

$$-K_2^{-}=\frac{(D_{11}-D_{22})-\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}-2D_{21}C_1^{\circ}/C_2^{\circ}}{2\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}} \qquad (13)$$

$$\sigma_+=\frac{(D_{22}+D_{11})+\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}}{2(D_{11}D_{22}-D_{12}D_{21})} \qquad (14)$$

$$\sigma_-=\frac{(D_{22}+D_{11})-\sqrt{(D_{22}-D_{11})^2+4D_{12}D_{21}}}{2(D_{11}D_{22}-D_{12}D_{21})} \qquad (15)$$

The surface concentrations C_1° and C_2° are determined by extrapolation of the dye distribution curves in the cellophane roll. The four diffusion coefficients should be determined simultaneously. However, the calculation of these coefficients from the dye distribution curve is not possible. It is assumed that the main diffusion coefficients, D_{11} and D_{22}, are the diffusion coefficients of each single dyeing whose surface concentration is equal to that in the mixture dyeing. Therefore, the cross-term diffusion coefficients, D_{12} and D_{21}, are determined by the trial and error from Eqs. 8—15, using the values of C_1°, C_2°, D_{11} and D_{22} obtained above.

Results

Single Dyeing.—The results for single dyeings are shown in Tables I (Benzopurpurine 4B) and II (Sky Blue 6B), which show the surface dye concentrations and the diffusion coefficients of single dyeing. According to the theory of activated diffusion, the observed diffusion coefficient at a given temperature is given by the equation

$$\log D=\log D_0-E/2.303RT \qquad (16)$$

where E is the apparent activation energy of the diffusion.

From the experiments at various dye concentrations, the apparent activation energy of

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* s. c.=Swollen cellophane.

9) M. Sekido and K. Matsui, Meeting of the Society of Textile and Cellulose Industries, Japan (1959).

10) R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *J. Am. Chem. Soc.*, **77**, 5235 (1955).

11) H. Fujita and L. J. Gosting, ibid., **78**, 1099 (1956).

TABLE I. THE DIFFUSION COEFFICIENTS AND THE SURFACE CONCENTRATIONS OF BENZOPURPURINE 4B

(5.0×10^{-5} mol. dye/l. dyeing liquor)

Temp. °C	NaCl concn. mol./l.	$C_0\times10^5$ mol./cm³ s.c.	$D\times10^8$ cm²/min.
90	0.01	0.89	3.5
	0.02	1.1	4.0
	0.03	1.7	4.4
	0.04	1.8	5.0
85	0.03	1.8	2.1
80	0.03	2.0	1.7
75	0.03	2.2	1.3

TABLE II. THE DIFFUSION COEFFICIENTS AND THE SURFACE CONCENTRATIONS OF SKY BLUE 6B

(5.0×10^{-5} mol. dye/l. dyeing liquor)

Temp. °C	NaCl concn. mol./l.	$C_0\times10^6$ mol./cm³ s.c.	$D\times10^8$ cm²/min.
90	0.01	1.3	3.9
	0.02	2.5	5.6
	0.03	2.7	5.8
	0.04	5.6	5.8
85	0.03	4.3	5.1
80	0.03	5.2	3.1
75	0.03	6.8	2.5

the diffusion at a certain surface concentration can be obtained. Figures 1 and 2 show the relation between the logarithm of the diffusion coefficient and the reciprocal of the absolute temperature ($1/T$ °K^{-1}) at a constant surface concentration, and some numerical results obtained from these figures are given in Table III.

Mixture Dyeing*.—The dye distributions at

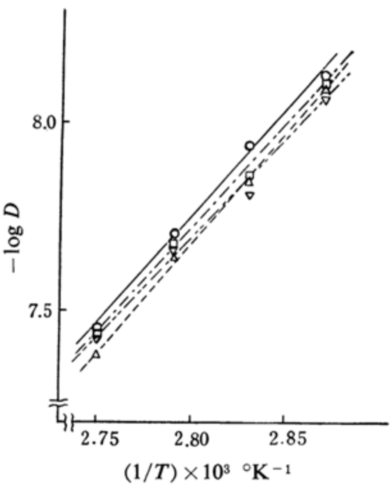

Fig. 1. Effect of temperature on diffusion coefficient of Benzopurpurine 4B.
—○— 0.01; --△-- 0.02; -·-□-·- 0.03; -··-▽-··- 0.04 mol. NaCl/l.

* Dye 1 denotes Benzopurpurine 4B and dye 2 denotes Sky Blue 6B.

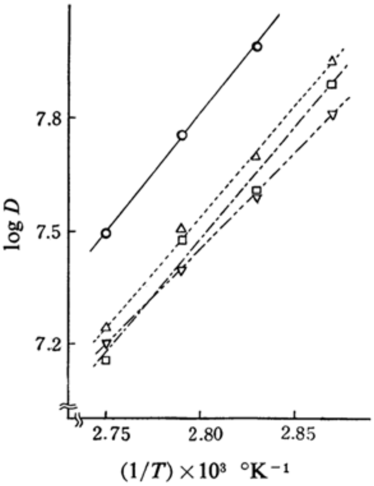

Fig. 2. Effect of temperature on diffusion coefficient of Sky Blue 6B.
—○— 0.01; --△-- 0.02; -·-□-·- 0.03; -··-▽-··- 0.04 mol. NaCl/l.

TABLE III. APPARENT ACTIVATION ENERGY OF DIFFUSION

	E kcal./mol.	$C_0\times10^6$ mol./cm³ s.c.	NaCl concn. mol./l.
Benzopurpurine 4B	25.6	8.	0.01
	26.8	11.	0.02
	25.2	14.	0.03
	24.2	16.	0.04
Sky Blue 6B	28.5	1.3	0.01
	27.2	2.7	0.02
	26.4	3.6	0.03
	23.8	4.6	0.03

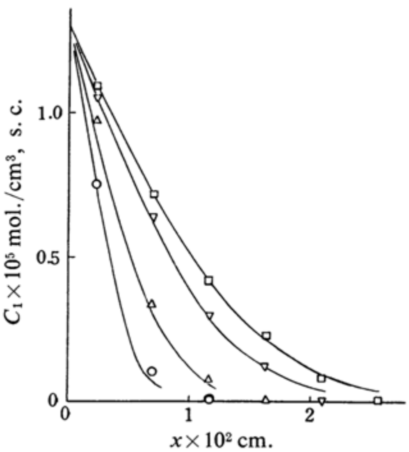

Fig. 3. The distributions of Benzopurpurine 4B at various times of mixture dyeing.
○ 187; △ 540; ▽ 1448; □ 2130 min.
—— theoretical curve.
each dye concn. = 5.0×10^{-5} mol./l., 90°C; 0.03 mol. NaCl/l.

TABLE IV. FOUR DIFFUSION COEFFICIENTS AND SURFACE CONCENTRATIONS IN MIXTURE DYEING* (at 90°C)

NaCl concn. mol./l.	D_{11}	D_{22} ($\times 10^8$	D_{12} cm^2/min.)	D_{21}	$C_1^\circ \times 10^5$	$C_2^\circ \times 10^6$ (mol./cm^3 s. c.)
0.01	2.9	2.0	−0.01	0.10	0.49	0.38
0.02	3.1	2.3	−0.01	0.40	0.97	0.96
0.03	3.3	3.0	−0.01	0.80	1.3	1.6
0.04	3.3	4.0	−0.09	1.1	1.5	2.2

TABLE V. FOUR DIFFUSION COEFFICIENTS AND SURFACE CONCENTRATIONS IN MIXTURE DYEING* (0.03 mol. NaCl/l.)

Temp. °C	D_{11}	D_{22} ($\times 10^8$	D_{12} cm^2/min.)	D_{21}	$C_1^\circ \times 10^5$	$C_2^\circ \times 10^6$ (mol./cm^3 s. c.)
85	2.5	1.8	-0.01_6	0.74	1.4_5	1.8
80	1.6	1.3	-0.04_4	0.57	1.6	2.2
75	1.2	0.80	-0.01_4	0.22	1.6	2.0

* Concentration of each dye $=5.0\times10^{-5}$ mol./l.

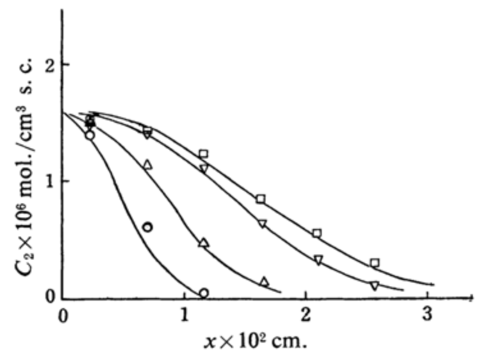

Fig. 4. The distributions of Sky Blue 6B at various times of mixture dyeing.
○ 187; △ 540; ▽ 1448; □ 2130 min.
—— theoretical curve
each dye concn. $=5.0\times10^{-5}$mol./l.; 90°C; 0.03 mol. NaCl/l.

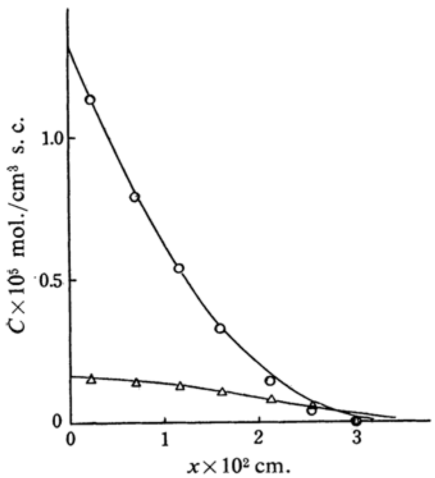

Fig. 5. Dye distributions in mixture dyeing.
○ Benzopurpurine 4B; △ Sky Blue 6B;
—— theoretical curve;
each dye concn. $=5.0\times10^{-5}$ mol./l.; 90°C; 3000 min.; 0.03 mol. NaCl/l.

various times in the dyeing process are shown in Figs. 3 (Benzopurpurine 4B) and 4 (Sky Blue 6B).

The salt effects on mixture dyeing were also examined at 90°C, the results are shown in Table IV. The dye distributions in one of these experiments are shown in Fig. 5, where the solid curves are theoretical curves derived from Eqs. 8 and 9.

The temperature effects on mixture dyeing at a certain sodium chloride concentration (3.0×10^{-2} mol./l.) are shown in Table V.

Discussion

Activation Energy of Diffusion.—The apparent activation energy of the diffusion of Sky Blue 6B, as determined by Boulton and Morton[12], is in the range of 15∼19 kcal./mol. for viscose rayon. These values are for a constant dye bath concentration. However, as the diffusion coefficient of a dye is a function of the dye content in a substrate, and since under the conditions of a constant dye bath concentration the surface dye concentration decreases with the increasing temperature, the activation energy of the diffusion should be estimated for a constant dye content, i. e., at a constant surface concentration.

The values we found for Sky Blue 6B, as shown in Table IV, are greater than those of Boulton and Morton[12]. These differences may be attributed to the concentration dependence of the diffusion coefficients. If the values of the activation energy of the diffusion for a constant dye bath concentration (5.0×10^{-5} mol./l.) are calculated, they are 22∼25 kcal./mol. for Benzopurpurine 4B and 13∼19 kcal./mol. for Sky Blue 6B. The values for Sky

12) J. Boulton and T. H. Morton, quoted by T. Vickerstaff, "The Physical Chemistry of Dyeing", 2nd Ed., Oliver & Boyd, London (1954), p. 268.

Blue 6B are similar to those of Boulton and Morton[12].

Mixture Dyeing.—As is shown in Figs. 3 (Benzopurpurine 4B) and 4 (Sky Blue 6B), the dye distributions in the mixture dyeing are considerably different from that in the single dyeing, and the surface concentration of each dye is maintained constant throughout the whole period of mixture dyeing.

Let us consider the case of Fig. 5. The surface concentration of each dye is smaller in the mixture dyeing than that in the single dyeing, irrespective of the constant dye concentrations in the dye bath. Clearly the diffusion of Sky Blue 6B cannot be described by means of Fick's law, as given in Eq. 1. Owing to the concentration dependence, the (main) diffusion coefficient of each dye should decrease with the decrease in surface concentration. If the main diffusion coefficients are obtained from the experiments of single dyeing and if the cross-term diffusion coefficients are estimated properly, as is mentioned in the theoretical section, the theoretical curves derived from Fqs. 8 and 9 agree well with the dye distributions of the mixture dyeing. The diffusion of Sky Blue 6B was greatly accelerated by the presence of Benzopurpurine 4B, as the value of the cross-term diffusion coefficient of blue dye is plus. In the case of Figs. 3 and 4, too, there are good agreements between the experimental results and the theoretical curves.

The effect of salt and temperature on mixture dyeing is very difficult to study, for the main diffusion coefficients and the surface concentrations vary with the salt concentration and temperature. According to the findings on the salt effect on mixture dyeing at 90°C, in which only the concentration of sodium chloride is varied from 0.01 to 0.04 mol./l., the interaction between two dyes will increase with an increase in the concentration of sodium chloride, for the absolute values of the cross-term diffusion coefficients change more than those of the main diffusion coefficients do. It is considered that the effect of a decrease in temperature is similar to that of an increase in salt concentration.

In mixture dyeing there may be two different interactions between two dyes, one in the dye bath and the other in the substrate. The interaction in the dye bath reduces the surface dye concentration below its normal value, as was studied earlier by Neale and Stringfellow[1] and by Horiki et al.[2,3] The cause of the interaction in the substrate may be that Sky Blue 6B is easy to diffuse, as a large amount of Benzopurpurine 4B adsorbed in the substrate reduces the available surface for the blue dye.

Summary

1. The single and mixture dyeing of Benzopurpurine 4B (C. I. 23500) and Sky Blue 6B (C. I. 24410) were examined kinetically.

2. The diffusion coefficient of each dye decreased with a decrease in the surface concentration. The apparent activation energy of diffusion at a constant surface concentration was evaluated.

3. In mixture dyeing, the dye distributions in the substrate were considerably different from that in the single dyeing, but there was good agreement between the dye distributions experimentally determined and those theoretically calculated in terms of the thermodynamics of irreversible processes.

4. The interaction between two dyes in the substrate increased with an increase in the sodium chloride concentration in the dye bath and with a decrease in the temperature.

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