*Studies on Mixture Dyeing. II. The Kinetics of a Mixture of Chrysophenine G and Sirius Red 4B**

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In the previous paper,[1] the mixture dyeing whose dyebath contained an equimolar mixture solution of Benzopurpurine 4B and Sky Blue 6B was kinetically investigated. There was a great difference in surface concentration between the two dyes owing to the great difference in affinity between them. Therefore, because of the sharp gradient of the concentration of Benzopurpurine 4B the interaction between the two dyes in the substrate, especially the effect of the blue dye on the diffusion of the red dye, could not be estimated quantitatively.

In this paper, the mixture dyeing of Chrysophenine G (C. I. Direct Yellow 12) and Sirius Red 4B (C. I. Direct Red 81), which are very similar to each other in dyeing property, has been studied; the single dyeings of these dyes have also been carried out in order to discuss quantitatively their behavior in the mixture dyeing.

First, the equilibrium adsorption from the single and mixture dyebath was investigated. Then, on the basis of the obtained results, the dyeing conditions for kinetic study were determined.

In order to estimate the effect of the yellow dye on the diffusion of the red dye, the surface concentration of the former dye was gradually increased at a constant surface concentration of the latter dye, and vice versa; diffusion experiments were then carried out. When both dyes had equal surface concentrations, the kinetics of mixture dyeing has been investigated. The temperature effect of mixture dyeing has also been studied.

Experimental

Materials.—A cellophane sheet made by the Tokyo Cellophane Co., Ltd., was used as the dyeing substrate. It was scoured with distilled water and conditioned in a desiccator with 50% sulfuric acid.

Purified dyes were used throughout. They were prepared from commercial dyes (Kayaku Chrysophenine GX (KYK) and Suprazo Red 4B (MDW)) by the method of Robinson and Mills.[2] The absence of colored impurities was verified by paper chromatography.

Equilibrium Dyeing.—The dyeings were carried out following the method of Horiki et al.[3] Pieces of the sample, weighing from 25 to 35 mg., were dyed in 200 ml. of dyeing liquor at 90, 85 and 80°C. The dyeing duration was one day (90°C) or two days (85 and 80°C). In the case of the single dyeing, the dye concentrations of the equilibrium dyebath were as shown in Figs. 1 and 2. Those of the mixture dyeing shown in Tables III, IV and V, were determined by a large number of preliminary experiments. After dyeing, the pieces of the sample

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1) Part I: M. Sekido and Z. Morita, This Bulletin, 35, 1375 (1962).

2) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.*, A131, 576 (1931).

3) Y. Horiki, Y. Tanizaki and N. Ando, This Bulletin, 33, 163 (1960).

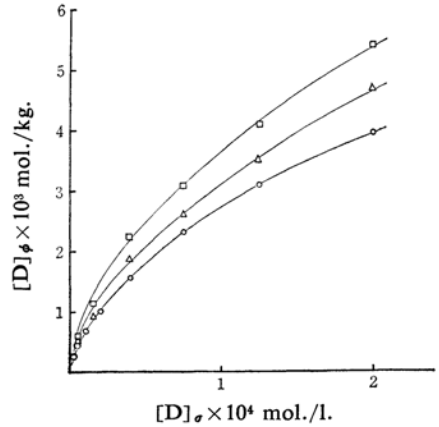

Fig. 1. Adsorption isotherms of Chrysophenine G.

NaCl: 3.0×10^{-2} mol./l.
—○— 90°C, —△— 85°C, —□— 80°C

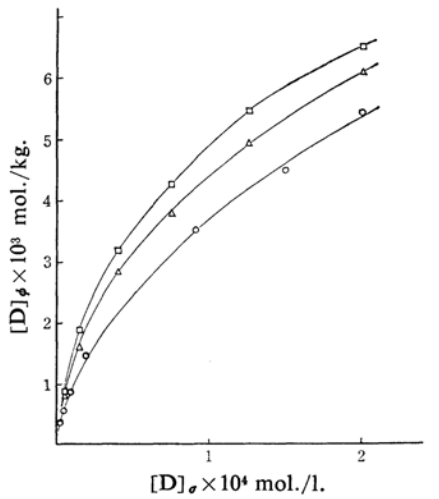

Fig. 2. Adsorption isotherms of Sirius Red 4B.

NaCl: 3.0×10^{-2} mol./l.
—○— 90°C, —△— 85°C, —□— 80°C

were quickly rinsed in a dilute sodium chloride aqueous solution, dried, and stripped in 25% aqueous pyridine. The strippings were analyzed by determining the optical densities at the wavelength of maximum absorption for each component by the use of a Hitachi EPB-V type spectrophotometer (405 and 520 mμ). The absorption spectra of the mixture dye in an aqueous pyridine solution were found to be additive. The concentration of sodium chloride was 0.03 mol./l. for every dyebath.

Diffusion.—The experimental methods were similar to those reported before.[1] The dyeing times were 500 min. (90°C), 750 min. (85°C) or 1000 min. (80°C). The dyeing condition, namely, the concentrations in the mixture dyeing, were determined by the results of the equilibrium adsorption.

Theoretical*

Dyeing Equilibrium.—The adsorption isotherms are obtained from the equilibrium dyeing measurements. According to Vickerstaff,[4] the isotherms are also derived from the theoretical considerations for any particular dyebath and substrate system. The standard affinity of direct dye anions for the substrate, $\Delta\mu^0$ (kcal./mol.), can be calculated by

$$-\Delta\mu^0=\boldsymbol{R}T\ln\frac{[\mathrm{D}]_\phi[\mathrm{Na}]_\phi{}^z}{V^{z+1}}-\boldsymbol{R}T\ln[\mathrm{D}]_\sigma[\mathrm{Na}]_\sigma{}^z \quad (1)$$

$$[\mathrm{Na}]_\phi=[\mathrm{D}]_\phi\left\{\frac{z}{2}+\left(\frac{z^2}{4}+\frac{V^2[\mathrm{Na}]_\sigma[\mathrm{Cl}]_\sigma}{[\mathrm{D}]_\phi{}^2}\right)^{1/2}\right\} \quad (2)$$

where $[\mathrm{D}]_\phi$ (mol./kg.) denotes the concentration of adsorbed dye anions in the substrate at equilibrium; $[\mathrm{Na}]_\phi$ (mol./kg.), the concentration of the sodium ions in the substrate at equilibrium; $[\mathrm{Na}]_\sigma$ and $[\mathrm{Cl}]_\sigma$ (mol./l.), the concentrations of the sodium and the chloride ions in the dyebath at equilibrium; z, the valency of the dye anions; $\boldsymbol{R}$, the gas constant; T, the absolute temperature, and V (l./kg.), the internal volume of the substrate. In this case, the volume term was taken to be 0.45.

Kinetics.—The theory of diffusion has been reported on before.[1] The distribution of Chrysophenine G and Sirius Red 4B in the substrate in the mixture dyeing, as shown in Results and Discussion, is similar in shape to that in the single dyeing. The diffusion equation of mixture dyeing, therefore, may be given by

$$\frac{\partial C_1}{\partial t}=D_{11}\frac{\partial^2C_1}{\partial x^2}+D_{12}\frac{\partial^2C_2}{\partial x^2}\approx D_1'\frac{\partial^2C_1}{\partial x^2} \quad (3)$$

$$\frac{\partial C_2}{\partial t}=D_{21}\frac{\partial^2C_2}{\partial x^2}+D_{22}\frac{\partial^2C_2}{\partial x^2}\approx D_2'\frac{\partial^2C_2}{\partial x_2} \quad (4)$$

where D_1' and D_2' (cm^2/min.) denote the apparent diffusion coefficient of each dye in the mixture dyeing. The other symbols are as given before.[1] These six diffusion coefficients have been calculated by the same methods as in the previous paper.[1]

Results and Discussion

Single Dyeing.—The adsorption isotherms of the two dyes at 90, 85 and 80°C are shown in Figs. 1 and 2, and the standard affinity, calculated by Eqs. 1 and 2, in Table I. The

* Chrysophenine G denotes dye 1 and Sirius Red 4B, dye 2; they are shown by subscripts such as D_{11} $[\mathrm{D}_2]_\phi$.

4) T. Vickerstaff, "The Physical Chemistry of Dyeing," 2nd ed., Oliver and Boyd, London (1954), p. 194.

TABLE I. STANDARD AFFINITY OF DIRECT DYES

Temp., °C	Chrysophenine G	Sirius Red 4B
90	$-(3.40\pm0.06)$	$-(3.73\pm0.06)$
85	$-(3.51\pm0.07)$	$-(3.90\pm0.07)$
80	$-(3.62\pm0.06)$	$-(3.94\pm0.07)$

diffusion coefficients at various surface concentrations are shown in Tables III, IV and V. The surface concentration, C_i^0, in diffusion experiments are assumed to be equal to the equilibrium adsorption, $[D_i]_\phi$, obtained from Figs. 1 and 2 for the same concentration in a dyebath. These results show that the two dyes have similar dyeing properties, although Chrysophenine G has a little larger diffusion coefficient and a little lower affinity than Sirius Red 4B.

The activation energies of diffusion at a constant surface concentration are given in Table II. They decrease with an increase in the surface concentration.

TABLE II. APPARENT ACTIVATION ENERGY OF DIFFUSION

	$C_0\times10^3$	E
Chrysophenine G	2.5	9.89
	3.0	8.35
	3.5	7.86
	4.5	5.79
Sirius Red 4B	2.5	16.9
	3.0	16.3
	3.5	14.7
	4.0	12.9

Mixture Dyeing.—The equilibrium adsorptions in mixture dyeing, which correspond to the expected dyeing condition described before, are as shown in Tables III, IV and V. In the kinetic study, three kinds of dyeing conditions and three dyeing temperatures are employed.

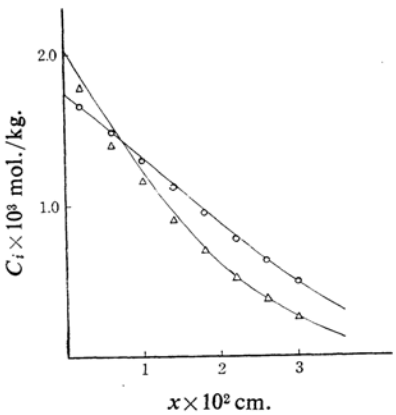

Fig. 3. Dye distribution in mixture dyeing.
○ Chryrophenine G, △ Sirius Red 4B
—— Theoretical curve; $[D_1]_\sigma=9.40\times10^{-5}$, $[D_2]_\sigma=6.35\times10^{-5}$,
NaCl: 3.0×10^{-2} mol./l.; 90°C; 500 min.
(Cf. Table III, Exp. No. 1)

The surface concentration, C_i^0, in diffusion experiments was assumed, as in single dyeing, to be equal to the equilibrium adsorption from the same concentration in the dyebath. As shown in Fig. 3, the surface concentration in diffusion experiments is a little different from the equilibrium adsorption under the same conditions, but this difference does not affect the calculation of the cross-term diffusion coefficients.

When the surface concentration of yellow dye at 90°C is maintained constant and that of red dye is gradually increased, the apparent diffusion coefficient of yellow dye, D_1', increases gradually. In this case, because of the concentration dependence of the diffusion coefficient, D_{22} (the diffusion coefficient of the red dye) increases with an increase in the surface concentration. D_{11} (that of the yellow dye) may not increase for the same reason. However, D_1' increases gradually with an increase in $[D_2]_\phi(=C_2^0)$. This, therefore, may be due to the effect of red dye on the diffusion of yellow dye. The diffusion of red dye may also be affected by yellow dye. As the surface concentration of the yellow dyes, however, is maintained constant, the yellow dyes may be almost identical in their effect on the diffusion of red dye, as Table III shows.

When the surface concentration of red dye is maintained constant, the reverse phenomenon is observed; namely, D_2' increases gradually. The effect of yellow dye on the diffusion of red dye seems to be smaller than in the reverse case. Such a situation is also observed when the surface concentrations of the two dyes are equal; these phenomena may be interpreted by means of the combination effect of the two dyeing conditions mentioned above.

D_{11}, D_{12}, D_{21} and D_{22} should be estimated simultaneously. As has been stated before, D_{11} and D_{22} determined by the single dyeing. Because of the activity of the dye and other factors, D_{11} and D_{22} may vary with the concentration of the two respective dyes. Although the concentration dependence of these diffusion coefficients has been investigated by O'Donnell and Gosting,[5] it can not be estimated from these experimental results with adequate experimental accuracy. As the absolute values of D_{12} are larger than those of D_{21}, and as D_{21} approximates to zero, it is considered, as has been stated before, that the effect of yellow dye on the diffusion of red dye is smaller than in the reverse case.

5) I. J. O'Donnell and L. J. Gosting, "The Structure of Electrolyte Solutions," Ed. by W. J. Hamer, John Wiley & Sons, Inc., New York (1959), Chap. 11.

Table III. Mixture dyeing at 90°C

Exp. No.	$[D_1]_\sigma$ $\times 10^4$	$[D_2]_\sigma$ $\times 10^4$	$[D_1]_\phi$ $\times 10^3$	$[D_2]_\phi$ $\times 10^3$	D_{11} $\times 10^7$	D_{12} $\times 10^7$	D_{21} $\times 10^7$	D_{22} $\times 10^7$	D_1' $\times 10^6$	D_2' $\times 10^7$	
1	0.94_0	0.63_5	2.01	2.35	6.5	3.0	-0.012_5	5.2	1.10	5.51	
2	1.02	0.82_0	1.96	2.69	6.5	2.8	−0.049	5.7	1.31	5.96	
3	1.08	1.04	2.00	3.20	6.5	2.5	−0.007	6.1	1.37	6.13	$[D_1]_\phi$=const.
4	1.14	1.27	1.93	3.45	6.5	2.3	−0.002	6.2	1.50	6.35	
5	1.20	1.52	1.94	3.81	6.5	2.1	−0.001	6.3	1.58	7.28	
6	1.17	0.51_0	2.43	2.09	7.2	3.5	−0.44	4.7	1.25	5.59	
7	1.45	0.56_0	2.71	2.08	7.8	3.9	−0.61	4.7	1.26	5.38	
8	1.59	0.57_8	2.90	2.07	8.4	4.5	-0.75_9	4.7	1.32	6.24	$[D_2]_\phi$=const.
9	1.72	0.60_3	3.10	2.10	8.9	5.0	−0.88	4.7	1.38	6.75	
10	1.97	0.62_5	3.51	2.09	9.6	5.6	-1.07_1	4.7	1.40	6.74	
11	0.88_5	0.46_5	2.03	1.96	6.5	3.2	-0.27_5	4.6	1.25	5.76	
12	1.26	0.72_3	2.46	2.50	7.2	3.4	-0.23_0	5.4	1.37	6.13	
13	1.53	0.88_0	2.60	2.60	7.6	3.5	-0.27_7	5.6	1.52	6.58	$[D_1]_\phi=[D_2]_\phi$
14	2.31	1.39	3.20	3.16	8.9	4.2	-0.45_0	6.1	1.65	7.19	
15	2.82	1.75	3.60	3.60	9.8	5.1	-0.55_0	6.4	1.74	8.96	

Table IV. Mixture dyeing at 85°C

Exp. No.	$[D_1]_\sigma$ $\times 10^5$	$[D_2]_\sigma$ $\times 10^5$	$[D_1]_\phi$ $\times 10^3$	$[D_2]_\phi$ $\times 10^3$	D_{11} $\times 10^7$	D_{22} $\times 10^7$	D_1' $\times 10^7$	D_2' $\times 10^7$	
1	8.22	5.63	2.25	2.61	6.0	4.0	8.7	4.5	
2	8.71	6.75	2.27	2.89	6.0	4.3	10.0	5.0	
3	9.13	8.15	2.34	3.29	6.0	4.7	9.3	4.2	$[D_1]_\phi$=const.
4	9.50	9.50	2.29	3.47	6.0	4.9	8.8	4.5	
5	9.95	12.5	2.27	4.13	6.0	5.4	13.0	4.9	
6	11.6	16.8	2.27	4.80	6.0	5.9	16.0	5.8	
7	7.46	4.25	2.07	2.12	5.5	3.5	8.7	3.9	
8	9.95	5.67	2.45	2.47	6.4	3.9	8.7	3.8	
9	12.4	7.75	2.64	2.79	6.9	4.2	13.0	4.8	$[D_1]_\phi=[D_2]_\phi$
10	19.8	13.6	3.71	3.80	8.9	5.2	14.0	5.6	
11	25.1	17.5	4.16	4.18	9.6	5.5	16.0	6.6	

Table V. Mixture dyeing at 80°C

Exp. No.	$[D_1]_\sigma$ $\times 10^4$	$[D_2]_\sigma$ $\times 10^5$	$[D_1]_\phi$ $\times 10^3$	$[D_2]_\phi$ $\times 10^3$	D_{11} $\times 10^7$	D_{22} $\times 10^7$	D_1' $\times 10^7$	D_2' $\times 10^7$	
1	1.00	5.10	3.22	2.79	6.8	2.8	7.5	3.3	
2	1.24	5.46	3.64	2.76	7.7	2.8	7.8	3.3	
3	1.48	5.77	4.14	2.72	8.4	2.8	8.1	3.7	$[D_2]_\phi$=const.
4	1.75	6.18	4.43	2.72	8.7	2.8	11.0	3.5	
5	2.02	6.55	4.96	2.78	9.0	2.8	10.0	3.6	
6	2.28	6.90	5.23	2.69	9.1	2.8	10.0	3.5	
7	0.79_0	4.75	2.52	2.54	5.2	2.7	6.2	2.9	
8	1.03	6.35	3.02	2.95	6.4	2.9	8.3	3.3	
9	1.32	8.35	3.40	3.43	7.2	3.2	12.0	4.0	$[D_1]_\phi=[D_2]_\phi$
10	1.65	11.1	4.03	4.00	8.3	3.4	8.9	3.4	
11	2.00	14.0	4.11	4.10	8.4	3.5	6.7	3.5	
12	2.49	18.9	4.74	4.75	9.0	3.7	9.0	4.1	

The distributions of these dyes in the substrate are very different from those in the mixture of Benzopurpurine 4B and Sky Blue 6B. This may be explained as follows. Chrysophenine G and Sirius Red 4B are similar to each other in distribution, while Benzopurpurine 4B and Sky Blue 6B are not. It follows that the effect of the two dyes on the diffusion of each dye is smaller in the former case than in the latter and that the dye distributions in

the present experiments, as shown in Fig. 3, may be Fickian. However, as Fig. 3 shows, the distribution of two dyes in the substrate agrees well with the theoretical curves in the previous paper.[1] Therefore, the unusual distribution of Sky Blue 6B may not be a particular one, and the shape of the dye distribution in the mixture dyeing may be determined by the value of the diffusion coefficients of the dye and the ratio of the surface concentrations; i.e., the dye distribution in the mixture dyeing may be Fickian only when the two dyes are similar to each other in dyeing property.

At 85°C, the dyeing condition of the constant surface concentration of yellow dye and the equal surface concentration of the two dyes are employed. The results are shown in Table IV. At 80°C, the dyeing condition of the constant surface concentration of red dye and the equal surface concentration of the two dyes are employed; the results are shown in Table V. Similar phenomena such as those at 90°C, are observed. As the results exhibit a little scatter, the cross-term diffusion coefficients have not been calculated.

Judging from the difference between D_1' and D_{11} or D_2' and D_{22}, the temperature effect on mixture dyeing seems to decrease with a decrease in the temperature. This is inconsistent with the cases of Benzopurpurine 4B and Sky Blue 6B. This temperature effect is considered to be caused by various complicated factors, such as the activity and the affinity of dye, which vary with the temperature. Therefore, it may not be possible to discuss it simply. The absorption spectra of the dye mixture in the substrate were additive, even in the case of a mixture of Chrysophenine G and Sky Blue 6B, in contrast with those in an aqueous solution.[6] Therefore, in the substrate, there may not be such a strong interaction to vary the absorption spectra as in a solution, and so the same complex between two dyes as in a solution may not result. The main factor influencing the diffusion in mixture dyeing may be a competition of available surfaces in the substrate. Then the dye with the smaller diffusion coefficient or with the larger affinity has a more profound effect on the diffusion of the dye with a larger diffusion coefficient or with a smaller affinity than in the reverse case. The results of these experiments confirm these hypotheses.

Summary

1) The single and mixture dyeing of Chrysophenine G (C. I. Direct Yellow 12) and Sirius Red 4B (C. I. Direct Red 81) have been examined kinetically.

2) The affinity and the diffusion coefficient of each dye at 90, 85 and 80°C have been evaluated. The apparent activation energy of diffusion at a constant surface concentration has been calculated.

3) In the mixture dyeing, although the apparent diffusion coefficient of each dye became larger than that in the single dyeing, whose surface concentration was similar to that in the mixture dyeing, the dye with the smaller diffusion coefficient had a more profound effect on the diffusion of the dye with the larger diffusion coefficient than in the reverse case.

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6) M. Sekido and Z. Morita, unpublished work.