

Studies on Mixture Dyeing. IV. Equilibrium Adsorption of Direct Dyes

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Synopsis

Chrysophenine G (C.I. Direct Yellow 12), Benzopurpurine 4B (Red 2), Sirius Red 4B (Red 81), Sirius Supra Blue BRR (Blue 71) and Sky Blue 6B (Blue 1) were selected as typical direct dyes, and the equilibrium adsorptions on cellulose (Cellophane) from the 1:1 and 2:1 molar mixture dye baths were investigated at 90° and 70°C. The standard affinity in mixture dyeing was obtained by the equation derived from the assumption of monodispersed and diffusive adsorption. The standard affinity in mixture dyeing was nearly equal to that in single dyeing, except for the Chrysophenine G-Sky Blue 6B system. However, judging from the fiber and solution log sum plots, there was a definite difference between mixture and single dyeing. It was explained by the change of activity of dye and sodium ions on substrate followed by the marked change of the total adsorption. The adsorption behavior of direct dyes is discussed in detail from the viewpoint of concentration dependence of the activity coefficient of dye and sodium ions on the substrate.

INTRODUCTION

The thermodynamic considerations of dyeing processes were summarized by Vickerstaff,¹ with modifications and developments thereof. In the calculation of the standard affinity of a direct dye for cellulose, the assumption was made that (1) the activity of all components is equal to the concentration, or the dye and neutral salt added perfectly ionize in both cellulose and dyebath phases, and (2) the internal volume of cellulose is constant for all the components. The validity of this assumption has been discussed from the slope of the log sum plot of ionic species in the cellulose and in the dyebath. (Theoretically the slope is unity.)

Marshall and Peters attributed the deviation of the slope from the theoretical value to the aggregation of dye in the substrate.² Nakagaki and Müller corrected the deviation by the activity coefficient of dye ion,^{3,4} Urahata, by the valency of the dye ions,⁵ and Standing,⁶ Holmes,⁷ Horiki,⁸ and Daruwalla and D'Silva,⁹ by the volume term. However, the absolute value of the activity of dye and salt ions in the substrate and that of internal volume have not yet been evaluated experimentally. Unless either

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of them is evaluated, the deviation of the slope of the log sum plot cannot be discussed quantitatively.

Inasmuch as a small difference has been observed by many chemists in the standard affinities of direct dyes, the corresponding data of single dyeing needed to discuss their behavior in mixture dyeing should be observed by the use of the same substrates (Cellophane).

The dyes to be used should have as wide a chemical structure as possible. For the present paper, five typical dyes (cf. Table I) were selected according to Neale and Stringfellow's investigation. These dyes may be assumed to be representative so far as their shape, chemical structure, dyeability, and molecular weight are concerned.

TABLE I
Direct Dye Samples

No.	Name	C.I. Direct	Abbreviation
1	Chrysophenine G	Yellow 12	D ₁
2	Benzopurpurine 4B	Red 2	D ₂
3	Sirius Red 4B	Red 81	D ₃
4	Sirius Supra Blue BRR	Blue 71	D ₄
5	Sky Blue 6B	Blue 1	D ₅

In single dyeing, the differences in adsorption behavior among these dyes are discussed in detail from the viewpoint mentioned above.

The mixture adsorption of direct dyes has been studied by Neale and Stringfellow¹⁰ and Horiki et al.^{8,11} Neale and Stringfellow observed that in a mixture of Chrysophenine G and Sky Blue 6B, the total dye adsorption from the mixture is less than the adsorption from Sky Blue 6B alone. They concluded that complex formation between dyes in the dye bath was the main factor which influenced the mixture dyeing. Horiki et al. supported this conclusion. But a theoretical equation by which the standard affinities in mixture adsorption can be calculated and a systematic study of mixture adsorption have not yet been presented.

In this paper, the theoretical equation from which the standard affinity in mixture dyeing can be calculated is derived. The mixture adsorptions are determined from the binary dye bath of the 1:1 and 1:2 molar ratio, and the standard affinities are calculated by equations. The factors influencing mixture dyeing are discussed in comparison with single dyeing.

THEORETICAL

Single Dyeing

It is assumed that the dye anions are diffusely adsorbed and ionized in both fiber and dye bath phases. The standard affinity, $-\Delta\mu_i^0$, of the dye anion is given¹ by

$$-\Delta\mu_i^0 = RT \ln \frac{[D_i]_\phi [Na]_\phi^{Z_i}}{V^{Z_i+1}} - RT \ln [D_i]_\sigma [Na]_\sigma^{Z_i} \quad (1)$$

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

where $[D_i]$ denotes the concentration of dye anion; $[Na]$, that of sodium ion; $[Cl]$, that of chloride ion; Z_i , the valency of the dye anion; R , the gas constant; T , the absolute temperature; subscript i denotes the i -th dye; and subscripts ϕ and σ , the fiber and dye bath, respectively. Although all the concentrations should be described by activity when theoretically treated, little is known about the activity of dye anions, much less about the determination of activity of dye anions in the fiber phase. In this paper, also in mixture dyeing, it is assumed that the activities of various kinds of ions are equal to the stoichiometric concentrations, and all calculations were carried out.

Mixture Dyeing

In mixture dyeing, the standard affinity of dye i , $-\Delta\mu_{D_i}^0$, is also given by

$$-\Delta\mu_{D_i}^0 = RT \ln \frac{[D_i]_\phi [Na]_\phi^{Z_i}}{V^{Z_i+1}} - RT \ln [D_i]_\sigma [Na]_\sigma^{Z_i}. \quad (3)$$

It is assumed, as in the case of single dyeing, that dyes in solution or diffusely adsorbed upon the substrate ionize perfectly in both phases. The symbols are the same as in the single dyeing.

As sodium chloride is not adsorbed by the substrate, i.e., the chemical potential of sodium chloride is the same in the dye bath as in the substrate at equilibrium, the sodium ion concentration in the surface solution layer of substrate $[Na]_s$ has the following relationship:

$$[Na]_\sigma [Cl]_\sigma = [Na]_s [Cl]_s \quad (4)$$

where $[Cl]_s$ denotes the chloride ion concentration in the surface solution layer of the substrate.

From the principle of electrical neutrality, $[Na]_s$ must be

$$V[Na]_s = V[Cl]_s + \sum_i Z_i [D_i]_\phi. \quad (5)$$

Substituting for $[Cl]_s$ from eq. (4) gives

$$[Na]_s^2 = [Na]_\sigma [Cl]_\sigma + \frac{1}{V} \left(\sum_i Z_i [D_i]_\phi \right) [Na]_s \quad (6)$$

which, solved for $[Na]_s$, gives

$$[Na]_s = \frac{1}{V} \left(\sum_i Z_i [D_i]_\phi \right) \left\{ \frac{1}{2} + \left(\frac{1}{4} + \frac{V^2 [Na]_\sigma [Cl]_\sigma}{\left(\sum_i Z_i [D_i]_\phi \right)^2} \right)^{1/2} \right\}. \quad (7)$$

Substituting $V[\text{Na}]_s$ for $[\text{Na}]_\phi$ in eq. (7) gives $[\text{Na}]_\phi$:

$$[\text{Na}]_\phi = \left(\sum_i Z_i [\text{D}_i]_\phi \right) \left\{ \frac{1}{2} + \left(\frac{1}{4} + \frac{V^2 [\text{Na}]_s [\text{Cl}]_s}{\left(\sum_i Z_i [\text{D}_i]_\phi \right)^2} \right)^{1/2} \right\}. \quad (8)$$

The standard affinity of dye anions in mixture dyeing can be calculated by eqs. (3) and (8). In this paper, only mixture dyeing with two dye components has been investigated.

EXPERIMENTAL

Purified dyes were used throughout. These samples were the same as those used before.¹² They were purified from commercial dyes by the method of Robinson and Mills.¹³ The absence of colored impurities was checked by paper chromatography.

Cellophane (#350, Tokyo Cellophane Sheet Co., Ltd.), 25–40 mg scoured by distilled water and conditioned in a 50% sulfuric acid desiccator, was dyed under given conditions, dried, and extracted by 25% aqueous pyridine. The optical density of the extracts was measured by a Hitachi EPB-V-type spectrophotometer at the maximum wavelength of each component to obtain equilibrium adsorptions. The volume of the dyebath was 100 or 200 ml, and dyeing time was one day at 90°C or two days at 70°C.

In mixture dyeing, the initial dyebath contained dye of 1:1 or 1:2 molar concentration ratio. At the low initial concentration, this ratio changed a little from its initial value. The dye combinations, which are shown below, were selected so that the absorption maximum wavelengths of absorption spectra of both dyes were not too close to each other. The molar ratios of the initial dyebath are given in parentheses:

1. Chrysophenine G and Benzopurpurine 4B (2:1)
2. Chrysophenine G and Sirius Red 4B (1:1 and 2:1)
3. Chrysophenine G and Sirius Supra Blue BRR (2:1)
4. Chrysophenine G and Sky Blue 6B (1:1 and 2:1)¹⁹
5. Benzopurpurine 4B and Sirius Supra Blue BRR (1:1)
6. Benzopurpurine 4B and Sky Blue 6B (1:1)
7. Sirius Red 4B and Sirius Supra Blue BRR (1:1)
8. Sirius Red 4B and Sky Blue 6B (1:1)
9. Sirius Supra Blue BRR and Sky Blue 6B (1:1)

RESULTS AND DISCUSSIONS

Single Dyeing

The adsorption of five direct dyes is shown in Figures 1 and 2 by fiber and solution log sum. At 90° and 70°C, the order of the slope is:

Sirius Red 4B < Chrysophenine G < Benzopurpurine 4B < Sirius Supra Blue BRR < Sky Blue 6B.

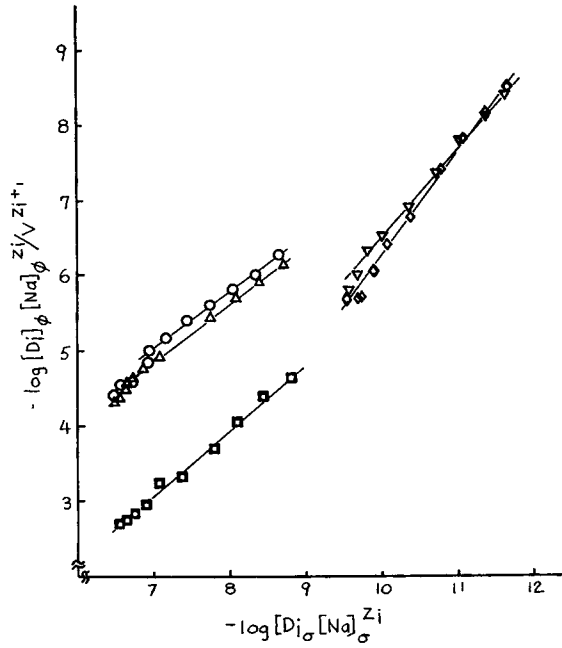


Fig. 1. Equilibrium adsorption of direct dyes (single dyeing) at 90°C: (O) D₁; (□) D₂; (Δ) D₃; (∇) D₄; (◇) D₅; NaCl concentration, 0.03 mole/l.

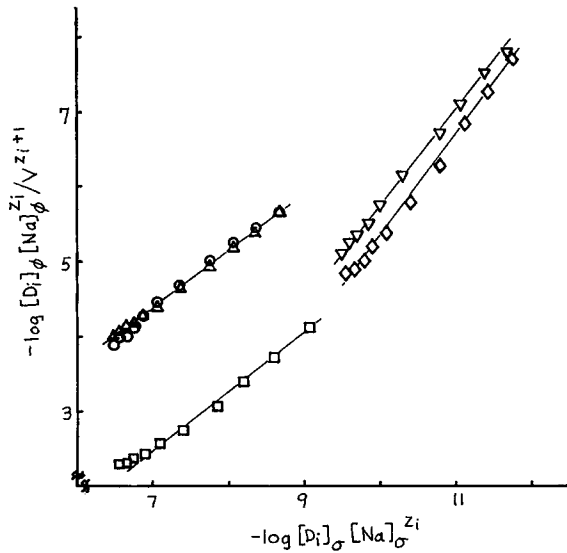


Fig. 2. Equilibrium adsorption of direct dyes (single dyeing) at 70°C: (O) D₁; (□) D₂; (Δ) D₃; (∇) D₄; (◇) D₅; NaCl concentration, 0.03 mole/l.

The theoretical slopes of these lines should be unity, if the real values of internal volume and activity of all ions were used. As stated before, these absolute values have not been experimentally evaluated. In this paper, the volume term was assumed to be 0.45 l./kg.^{14,15} Inasmuch as a substrate model, such that this value changes for each dye, or that the dye, or the sodium or chloride ion is independently adsorbed on different places in the substrate, is difficult to consider, especially in mixture dyeing, this assumption may be reasonable. A change in slope with temperature, which depends on the temperature effect of all ions, cannot be observed from Figures 1 and 2.

The difference in slope between dyes can be explained by the activity coefficient of dye ions but not by the change in the volume term. As the concentration of the dye ions is sufficiently small in comparison with that of the sodium ions, the difference between the concentration of sodium ions on the substrate and that in the dyebath may not be so large. On the other hand, the concentration difference of dye anions between both phases is considerably large, and the difference of the concentration dependence of activity coefficient of these dye and sodium ions between both phases cannot be neglected. Or, if the concentration dependence of the activity coefficient of the dye ions in the substrate is larger than that in solution, the slope value becomes smaller than the real one, and vice versa. The activity coefficient of the dye anions has a direct effect on that of the sodium ions, from eq. (2), and this effect brings about a similar effect on the slope. And, although the concentration dependence of the sodium ions in the substrate produces large additional effects on the fiber log sum, $\log [D_i]_\phi [Na]_\phi^{Z_i} / V^{Z_i+1}$, this is not the case in solution, as the concentration of sodium ions is much larger than that of dye ions. Then, the concentration dependence of the activity coefficient in the substrate is considered to be larger than that in solution. This is the reason why the slope of divalent dyes is smaller than that of tetravalent dyes. The activity coefficient of Sky Blue 6B behaves as a normal electrolyte of the between 1:2 and 1:4 valence type,^{16,17} and it is considered that the activity coefficient of Chryso-phenine G, and so on, behaves as one of the between 1:1 and 1:2 valence type. In general, the concentration dependence of 1:4 valence type electrolytes may be larger than that of 1:2 valence types. It is considered that, corresponding to the slope of the log sum plot, the concentration dependence of the activity coefficient is of the order Sirius Red 4B < Chryso-phenine G < Benzopurpurine 4B in divalent dyes, and Sirius Supra Blue BRR < Sky Blue 6B in tetravalent dyes. Similar treatments were made previously.⁸ The order of the slopes of Figures 1 and 2 may be understood by these considerations.

Mixture Dyeing

The adsorptions of direct dyes in admixture are shown in Tables III to X. Like previous investigation,^{8,10,11} they show that the adsorption behavior in mixture dyeing is very different from that in single dyeing.

TABLE II
Standard Affinity of Direct Dye Anions in Single Dyeing

Dye	$-\Delta\mu_i^0$, kcal/mole	
	at 70°C	at 90°C
D ₁	4.24 ± 0.05	3.40 ± 0.06
D ₂	7.24 ± 0.08	6.64 ± 0.04
D ₃	4.21 ± 0.06	3.73 ± 0.06
D ₄	6.57 ± 0.07	5.77 ± 0.07
D ₅	7.11 ± 0.08	6.02 ± 0.11

TABLE III
Equilibrium Adsorption of D₁ and D₂ in Admixture

Temp., °C	[D ₁] _σ , mole/l.	[D ₂] _σ , mole/l.	[D ₁] _φ , mole/kg	[D ₂] _φ , mole/kg	$-\Delta\mu_{D_1}^0$, kcal/mole	$-\Delta\mu_{D_2}^0$, kcal/mole
90	9.97 × 10 ⁻⁶	3.75 × 10 ⁻⁶	1.64 × 10 ⁻⁴	7.54 × 10 ⁻³	3.38	6.85
	1.99 × 10 ⁻⁵	8.43 × 10 ⁻⁶	3.64 × 10 ⁻⁴	1.03 × 10 ⁻²	3.71	6.75
	4.99 × 10 ⁻⁵	2.26 × 10 ⁻⁵	7.17 × 10 ⁻⁴	1.41 × 10 ⁻²	3.86	6.59
	9.96 × 10 ⁻⁵	4.46 × 10 ⁻⁵	1.31 × 10 ⁻³	1.77 × 10 ⁻²	4.11	6.57
	1.99 × 10 ⁻⁴	9.33 × 10 ⁻⁵	2.16 × 10 ⁻³	2.06 × 10 ⁻²	4.14	6.31
	4.99 × 10 ⁻⁴	2.43 × 10 ⁻⁴	4.00 × 10 ⁻³	2.30 × 10 ⁻²	4.10	5.88
70	9.87 × 10 ⁻⁶	2.92 × 10 ⁻⁶	7.45 × 10 ⁻⁴	1.20 × 10 ⁻²	4.81	7.53
	1.98 × 10 ⁻⁵	7.19 × 10 ⁻⁶	1.03 × 10 ⁻³	1.61 × 10 ⁻²	4.68	7.25
	4.97 × 10 ⁻⁵	2.16 × 10 ⁻⁵	1.76 × 10 ⁻³	2.07 × 10 ⁻²	4.73	6.98
	9.92 × 10 ⁻⁵	4.32 × 10 ⁻⁵	2.63 × 10 ⁻³	2.26 × 10 ⁻²	4.66	6.70
	1.98 × 10 ⁻⁴	9.25 × 10 ⁻⁵	4.13 × 10 ⁻³	2.47 × 10 ⁻²	4.65	6.39
	4.98 × 10 ⁻⁴	2.41 × 10 ⁻⁴	7.27 × 10 ⁻³	2.67 × 10 ⁻²	4.57	5.95

TABLE IV
Equilibrium Adsorption of D₁ and D₃ in Admixture

Temp., °C	[D ₁] _σ , mole/l.	[D ₃] _σ , mole/l.	[D ₁] _φ , mole/kg	[D ₃] _φ , mole/kg	$-\Delta\mu_{D_1}^0$, kcal/mole	$-\Delta\mu_{D_3}^0$, kcal/mole
90	4.93 × 10 ⁻⁶	4.89 × 10 ⁻⁶	3.79 × 10 ⁻⁴	5.76 × 10 ⁻⁴	3.81	4.12
	9.70 × 10 ⁻⁶	9.55 × 10 ⁻⁶	5.93 × 10 ⁻⁴	9.00 × 10 ⁻⁴	3.70	4.02
	2.49 × 10 ⁻⁵	2.48 × 10 ⁻⁵	9.38 × 10 ⁻⁴	1.50 × 10 ⁻³	3.36	3.71
	7.45 × 10 ⁻⁵	7.42 × 10 ⁻⁵	1.68 × 10 ⁻³	2.60 × 10 ⁻³	3.30	3.58
	1.49 × 10 ⁻⁴	1.49 × 10 ⁻⁴	2.83 × 10 ⁻³	2.93 × 10 ⁻³	3.28	3.30
	2.99 × 10 ⁻⁴	2.98 × 10 ⁻⁴	4.04 × 10 ⁻³	4.93 × 10 ⁻³	3.32	3.46
	9.92 × 10 ⁻⁵	4.92 × 10 ⁻⁵	5.20 × 10 ⁻⁴	5.10 × 10 ⁻⁴	3.54	4.03
	1.99 × 10 ⁻⁵	9.89 × 10 ⁻⁶	6.47 × 10 ⁻⁴	7.31 × 10 ⁻⁴	3.23	3.83
	4.98 × 10 ⁻⁵	2.48 × 10 ⁻⁵	1.34 × 10 ⁻³	1.32 × 10 ⁻³	3.23	3.72
	9.92 × 10 ⁻⁵	4.93 × 10 ⁻⁵	2.43 × 10 ⁻³	2.11 × 10 ⁻³	3.35	3.75
	1.99 × 10 ⁻⁴	9.94 × 10 ⁻⁵	3.46 × 10 ⁻³	2.73 × 10 ⁻³	3.26	3.59
		4.98 × 10 ⁻⁴	2.49 × 10 ⁻⁴	5.95 × 10 ⁻³	3.84 × 10 ⁻³	3.28
70	4.85 × 10 ⁻⁶	4.80 × 10 ⁻⁶	8.95 × 10 ⁻⁴	1.19 × 10 ⁻³	4.32	4.52
	9.74 × 10 ⁻⁶	9.68 × 10 ⁻⁶	1.28 × 10 ⁻³	1.78 × 10 ⁻³	4.18	4.41
	2.46 × 10 ⁻⁵	2.45 × 10 ⁻⁵	2.17 × 10 ⁻³	2.71 × 10 ⁻³	4.08	4.24
	7.47 × 10 ⁻⁵	7.36 × 10 ⁻⁵	3.82 × 10 ⁻³	4.26 × 10 ⁻³	4.00	4.07
	1.48 × 10 ⁻⁴	1.48 × 10 ⁻⁴	5.21 × 10 ⁻³	5.28 × 10 ⁻³	3.95	3.98
	2.98 × 10 ⁻⁴	2.98 × 10 ⁻⁴	7.15 × 10 ⁻³	6.50 × 10 ⁻³	3.88	3.82
	9.73 × 10 ⁻⁵	4.82 × 10 ⁻⁵	1.80 × 10 ⁻³	1.21 × 10 ⁻³	4.41	4.62
	1.97 × 10 ⁻⁵	9.76 × 10 ⁻⁶	2.17 × 10 ⁻³	1.62 × 10 ⁻³	4.13	4.41
	4.94 × 10 ⁻⁵	2.46 × 10 ⁻⁵	3.37 × 10 ⁻³	2.46 × 10 ⁻³	4.00	4.26
	9.86 × 10 ⁻⁵	4.91 × 10 ⁻⁵	4.89 × 10 ⁻³	3.19 × 10 ⁻³	3.98	4.16
	1.98 × 10 ⁻⁴	9.87 × 10 ⁻⁵	7.27 × 10 ⁻³	3.82 × 10 ⁻³	4.01	4.04
		4.96 × 10 ⁻⁴	2.48 × 10 ⁻⁴	1.09 × 10 ⁻²	5.11 × 10 ⁻³	3.98

TABLE V
Equilibrium Adsorption of D₁ and D₄ in Admixture

Temp., °C	[D ₁] _σ , mole/l.	[D ₄] _σ , mole/l.	[D ₁] _φ , mole/kg	[D ₄] _φ , mole/kg	-Δμ _{D₁} ⁰ , kcal/mole	-Δμ _{D₄} ⁰ , kcal/mole
90	9.91 × 10 ⁻⁶	4.78 × 10 ⁻⁶	5.74 × 10 ⁻⁴	1.47 × 10 ⁻³	3.88	5.45
	1.96 × 10 ⁻⁵	9.68 × 10 ⁻⁶	8.55 × 10 ⁻⁴	2.01 × 10 ⁻³	3.81	5.44
	4.98 × 10 ⁻⁵	2.43 × 10 ⁻⁵	1.34 × 10 ⁻³	3.10 × 10 ⁻³	3.71	5.60
	9.94 × 10 ⁻⁵	4.89 × 10 ⁻⁵	2.12 × 10 ⁻³	3.78 × 10 ⁻³	3.57	5.61
	1.99 × 10 ⁻⁴	9.86 × 10 ⁻⁵	3.07 × 10 ⁻³	4.69 × 10 ⁻³	3.71	5.68
4.98 × 10 ⁻⁴	2.48 × 10 ⁻⁴	5.33 × 10 ⁻²	6.15 × 10 ⁻³	3.76	5.85	
70	9.77 × 10 ⁻⁶	4.50 × 10 ⁻⁶	1.40 × 10 ⁻³	2.98 × 10 ⁻³	4.64	6.40
	1.97 × 10 ⁻⁵	9.44 × 10 ⁻⁶	1.80 × 10 ⁻³	3.56 × 10 ⁻³	4.47	6.28
	4.96 × 10 ⁻⁵	2.43 × 10 ⁻⁵	2.82 × 10 ⁻³	4.73 × 10 ⁻³	4.41	6.35
	9.83 × 10 ⁻⁵	4.83 × 10 ⁻⁵	3.75 × 10 ⁻³	5.34 × 10 ⁻³	4.29	6.27
	1.98 × 10 ⁻⁴	9.81 × 10 ⁻⁵	5.26 × 10 ⁻³	5.97 × 10 ⁻³	4.20	6.19
4.97 × 10 ⁻⁴	2.48 × 10 ⁻⁴	7.96 × 10 ⁻³	6.91 × 10 ⁻³	4.07	6.09	

TABLE VI
Equilibrium Adsorption of D₂ and D₄ in Admixture

Temp., °C	[D ₂] _σ , mole/l.	[D ₄] _σ , mole/l.	[D ₂] _φ , mole/kg	[D ₄] _φ , mole/kg	-Δμ _{D₂} ⁰ , kcal/mole	-Δμ _{D₄} ⁰ , kcal/mole
90	4.03 × 10 ⁻⁶	4.85 × 10 ⁻⁶	6.14 × 10 ⁻³	9.63 × 10 ⁻⁴	6.68	6.03
	8.55 × 10 ⁻⁶	9.79 × 10 ⁻⁶	8.81 × 10 ⁻³	1.29 × 10 ⁻³	6.69	6.31
	2.30 × 10 ⁻⁵	2.47 × 10 ⁻⁵	1.30 × 10 ⁻²	1.91 × 10 ⁻³	6.65	6.72
	6.90 × 10 ⁻⁵	7.41 × 10 ⁻⁵	1.79 × 10 ⁻²	2.64 × 10 ⁻³	6.46	6.90
	1.43 × 10 ⁻⁴	1.49 × 10 ⁻⁴	2.00 × 10 ⁻²	2.75 × 10 ⁻³	6.11	6.62
2.92 × 10 ⁻⁴	2.99 × 10 ⁻⁴	2.64 × 10 ⁻²	3.95 × 10 ⁻³	6.15	7.08	
70	3.33 × 10 ⁻⁶	4.72 × 10 ⁻⁶	1.06 × 10 ⁻²	1.76 × 10 ⁻³	7.30	7.09
	7.95 × 10 ⁻⁶	9.72 × 10 ⁻⁶	1.47 × 10 ⁻²	1.99 × 10 ⁻³	7.22	7.25
	2.20 × 10 ⁻⁵	2.46 × 10 ⁻⁵	1.97 × 10 ⁻²	2.45 × 10 ⁻³	7.04	7.39
	6.71 × 10 ⁻⁵	7.40 × 10 ⁻⁵	2.57 × 10 ⁻²	3.20 × 10 ⁻³	6.73	7.36
	1.41 × 10 ⁻⁴	1.49 × 10 ⁻⁴	2.98 × 10 ⁻²	3.74 × 10 ⁻³	6.54	7.42
2.88 × 10 ⁻⁴	2.99 × 10 ⁻⁴	3.38 × 10 ⁻²	4.07 × 10 ⁻³	6.25	7.23	

TABLE VII
Equilibrium Adsorption of D₂ and D₄ in Admixture

Temp., °C	[D ₂] _σ , mole/l.	[D ₄] _σ , mole/l.	[D ₂] _φ , mole/kg	[D ₄] _φ , mole/kg	-Δμ _{D₂} ⁰ , kcal/mole	-Δμ _{D₄} ⁰ , kcal/mole
90	3.97 × 10 ⁻⁶	4.88 × 10 ⁻⁶	7.20 × 10 ⁻³	8.22 × 10 ⁻⁴	6.88	6.05
	8.63 × 10 ⁻⁶	9.85 × 10 ⁻⁶	9.99 × 10 ⁻³	1.07 × 10 ⁻³	6.83	6.31
	2.30 × 10 ⁻⁵	2.48 × 10 ⁻⁵	1.45 × 10 ⁻²	1.64 × 10 ⁻³	6.79	6.73
	6.96 × 10 ⁻⁵	7.43 × 10 ⁻⁵	1.94 × 10 ⁻²	2.44 × 10 ⁻³	6.57	6.95
	1.44 × 10 ⁻⁴	1.49 × 10 ⁻⁴	2.30 × 10 ⁻²	2.97 × 10 ⁻³	6.38	7.01
2.92 × 10 ⁻⁴	2.99 × 10 ⁻⁴	2.73 × 10 ⁻²	3.81 × 10 ⁻³	6.19	7.10	
70	3.52 × 10 ⁻⁶	4.69 × 10 ⁻⁶	1.19 × 10 ⁻²	1.90 × 10 ⁻³	7.45	7.35
	7.66 × 10 ⁻⁶	9.68 × 10 ⁻⁶	1.65 × 10 ⁻²	2.22 × 10 ⁻³	7.45	7.59
	2.18 × 10 ⁻⁵	2.46 × 10 ⁻⁵	2.19 × 10 ⁻²	2.87 × 10 ⁻³	7.26	7.78
	6.71 × 10 ⁻⁵	7.38 × 10 ⁻⁵	2.75 × 10 ⁻²	4.09 × 10 ⁻³	6.95	7.89
	1.41 × 10 ⁻⁴	1.49 × 10 ⁻⁴	3.18 × 10 ⁻²	4.90 × 10 ⁻³	6.73	7.89
2.89 × 10 ⁻⁴	2.98 × 10 ⁻⁴	3.63 × 10 ⁻²	5.97 × 10 ⁻³	6.48	8.00	

TABLE VIII
Equilibrium Adsorption of D₃ and D₄ in Admixture

Temp., °C	[D ₃]σ, mole/l.	[D ₄]σ, mole/l.	[D ₃]φ, mole/kg	[D ₄]φ, mole/kg	-Δμ _{D₃} ⁰ , kcal/mole	-Δμ _{D₄} ⁰ , kcal/mole
90	4.92 × 10 ⁻⁶	4.79 × 10 ⁻⁶	5.26 × 10 ⁻⁴	1.44 × 10 ⁻³	4.31	5.41
	9.86 × 10 ⁻⁶	9.70 × 10 ⁻⁶	9.64 × 10 ⁻⁴	1.99 × 10 ⁻³	4.40	5.45
	2.48 × 10 ⁻⁵	2.46 × 10 ⁻⁵	1.27 × 10 ⁻³	2.88 × 10 ⁻³	4.13	5.45
	7.44 × 10 ⁻⁵	7.39 × 10 ⁻⁵	1.99 × 10 ⁻³	3.99 × 10 ⁻³	3.92	5.40
	1.49 × 10 ⁻⁴	1.49 × 10 ⁻⁴	2.78 × 10 ⁻³	5.12 × 10 ⁻³	3.82	5.53
	2.99 × 10 ⁻⁴	2.98 × 10 ⁻⁴	3.47 × 10 ⁻³	6.00 × 10 ⁻³	3.69	5.43
70	4.85 × 10 ⁻⁶	4.60 × 10 ⁻⁶	9.52 × 10 ⁻⁴	2.60 × 10 ⁻³	4.75	6.07
	9.80 × 10 ⁻⁶	9.49 × 10 ⁻⁶	1.27 × 10 ⁻³	3.25 × 10 ⁻³	4.61	6.02
	2.47 × 10 ⁻⁵	2.43 × 10 ⁻⁵	1.94 × 10 ⁻³	4.32 × 10 ⁻³	4.49	6.02
	7.41 × 10 ⁻⁵	7.32 × 10 ⁻⁵	2.73 × 10 ⁻³	5.67 × 10 ⁻³	4.23	5.97
	1.49 × 10 ⁻⁴	1.48 × 10 ⁻⁴	3.32 × 10 ⁻³	6.92 × 10 ⁻³	4.08	5.99
	2.99 × 10 ⁻⁴	2.98 × 10 ⁻⁴	4.08 × 10 ⁻³	7.72 × 10 ⁻³	3.85	5.80

TABLE IX
Equilibrium Adsorption of D₃ and D₅ in Admixture

Temp., °C	[D ₃]σ, mole/l.	[D ₅]σ, mole/l.	[D ₃]φ, mole/kg	[D ₅]φ, mole/kg	-Δμ _{D₃} ⁰ , kcal/mole	-Δμ _{D₅} ⁰ , kcal/mole
90	4.92 × 10 ⁻⁶	4.83 × 10 ⁻⁶	5.47 × 10 ⁻⁴	1.23 × 10 ⁻³	4.29	5.21
	9.87 × 10 ⁻⁶	9.71 × 10 ⁻⁶	8.29 × 10 ⁻⁴	1.91 × 10 ⁻³	4.11	5.06
	2.48 × 10 ⁻⁵	2.45 × 10 ⁻⁵	1.32 × 10 ⁻³	3.02 × 10 ⁻³	4.19	5.54
	7.44 × 10 ⁻⁵	7.38 × 10 ⁻⁵	2.05 × 10 ⁻³	4.64 × 10 ⁻³	3.88	5.73
	1.49 × 10 ⁻⁴	1.48 × 10 ⁻⁴	2.58 × 10 ⁻³	5.61 × 10 ⁻³	3.89	5.72
	2.99 × 10 ⁻⁴	2.98 × 10 ⁻⁴	3.26 × 10 ⁻³	6.87 × 10 ⁻³	3.75	5.73
70	4.87 × 10 ⁻⁶	4.57 × 10 ⁻⁶	9.16 × 10 ⁻⁴	3.09 × 10 ⁻³	4.81	6.37
	9.82 × 10 ⁻⁶	9.43 × 10 ⁻⁶	1.25 × 10 ⁻³	4.04 × 10 ⁻³	4.73	6.44
	2.47 × 10 ⁻⁵	2.42 × 10 ⁻⁵	1.72 × 10 ⁻³	5.40 × 10 ⁻³	4.57	6.49
	7.44 × 10 ⁻⁵	7.29 × 10 ⁻⁵	2.27 × 10 ⁻³	7.37 × 10 ⁻³	4.30	6.55
	1.49 × 10 ⁻⁴	1.47 × 10 ⁻⁴	2.68 × 10 ⁻³	8.96 × 10 ⁻³	4.13	6.58
	2.99 × 10 ⁻⁴	2.97 × 10 ⁻⁴	3.05 × 10 ⁻³	1.05 × 10 ⁻²	3.89	6.50

TABLE X
Equilibrium Adsorption of D₄ and D₅ in Admixture

Temp., °C	[D ₄]σ, mole/l.	[D ₅]σ, mole/l.	[D ₄]φ, mole/kg	[D ₅]φ, mole/kg	-Δμ _{D₄} ⁰ , kcal/mole	-Δμ _{D₅} ⁰ , kcal/mole
90	4.82 × 10 ⁻⁶	4.83 × 10 ⁻⁶	1.27 × 10 ⁻³	1.19 × 10 ⁻³	5.62	5.58
	9.79 × 10 ⁻⁶	9.75 × 10 ⁻⁶	1.56 × 10 ⁻³	1.86 × 10 ⁻³	5.64	5.77
	2.47 × 10 ⁻⁵	2.46 × 10 ⁻⁵	2.00 × 10 ⁻³	2.87 × 10 ⁻³	5.65	5.93
	7.43 × 10 ⁻⁵	7.37 × 10 ⁻⁵	2.63 × 10 ⁻³	4.71 × 10 ⁻³	5.82	6.25
	1.49 × 10 ⁻⁴	1.48 × 10 ⁻⁴	2.58 × 10 ⁻³	6.11 × 10 ⁻³	5.62	6.25
	2.99 × 10 ⁻⁴	2.98 × 10 ⁻⁴	2.84 × 10 ⁻³	8.19 × 10 ⁻³	5.66	6.42
70	4.81 × 10 ⁻⁶	4.51 × 10 ⁻⁶	1.26 × 10 ⁻³	3.21 × 10 ⁻³	6.04	6.73
	9.73 × 10 ⁻⁶	9.38 × 10 ⁻⁶	1.84 × 10 ⁻³	4.15 × 10 ⁻³	6.30	6.88
	2.47 × 10 ⁻⁵	2.41 × 10 ⁻⁵	2.16 × 10 ⁻³	5.66 × 10 ⁻³	6.28	6.95
	7.43 × 10 ⁻⁵	7.24 × 10 ⁻⁵	2.28 × 10 ⁻³	8.42 × 10 ⁻³	6.22	7.13
	1.49 × 10 ⁻⁴	1.47 × 10 ⁻⁴	3.75 × 10 ⁻³	9.34 × 10 ⁻³	6.52	7.15
	2.99 × 10 ⁻⁴	2.97 × 10 ⁻⁴	3.86 × 10 ⁻³	1.14 × 10 ⁻²	6.34	7.09

Neale and Stringfellow¹⁰ studied the equilibrium adsorption of binary direct dye mixtures by cotton, and considered three factors to influence mixture adsorption: (1) competition of dye anions for the available surface, (2) reduction of adsorption of each dye resulting from the increased surface charge and sodium ion concentration in the fiber, and (3) reduction

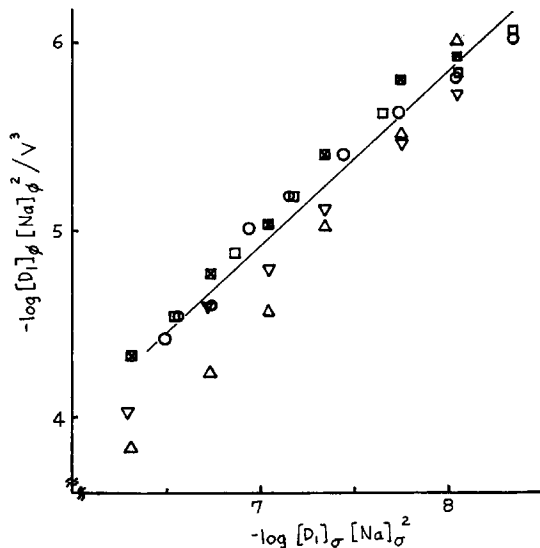


Fig. 3. Equilibrium adsorption of Chrysophenine G at 90°C: (O) single dyeing; (Δ) mixture with D₂; (□) D₃, 1:1; (■) D₃, 2:1; (▽) D₄; NaCl concentration, 0.03 mole/l.

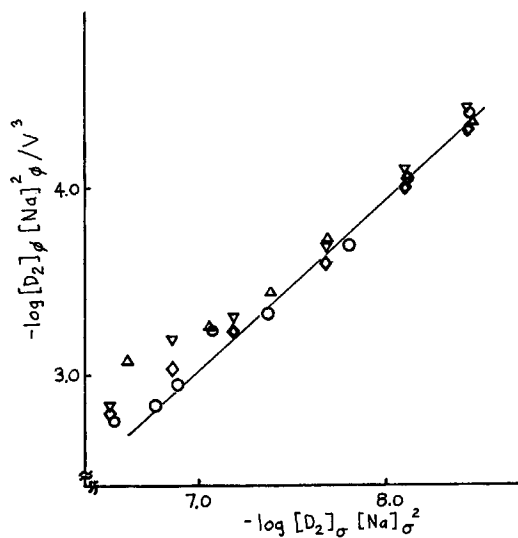


Fig. 4. Equilibrium adsorption of Benzopurpurine 4B at 90°C: (O) single dyeing; (Δ) mixture with D₁; (▽) D₄; (◇) D₅; NaCl concentration, 0.03 mole/l.

of available dye concentration resulting from their mutual interaction in solution.

It is considered that factor (1) plays a role in the sense that more than one dye is adsorbed on the same internal surface, resulting in reduction of the adsorption as factor (2), not in the sense that there is a limited available

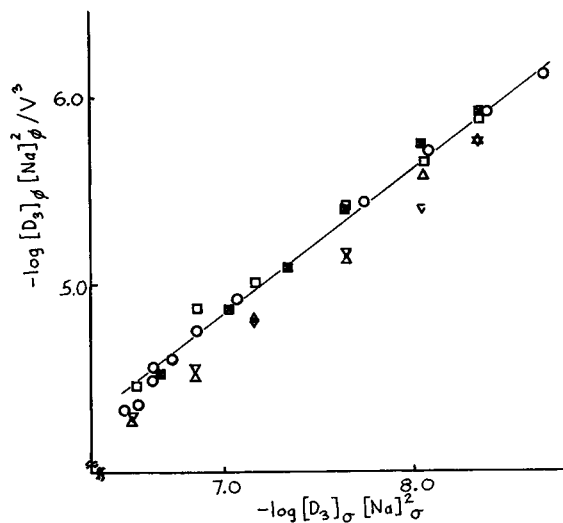


Fig. 5. Equilibrium absorption of Sirius Red 4B at 90°C: (O) single dyeing; (□) mixture with D₁, 1:1; (⊠) D₁, 1:2; (▽) D₄; (△) D₅; NaCl concentration, 0.03 mole/l.

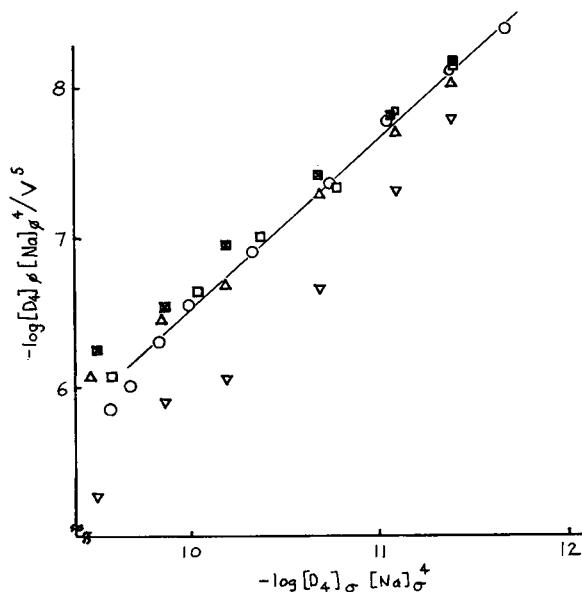


Fig. 6. Equilibrium adsorption Sirius Supra Blue BRR at 90°C: (O) single dyeing; (□) mixture with D₁; (▽) D₂; (⊠) D₃; (△) D₅; NaCl concentration, 0.03 mole/l.

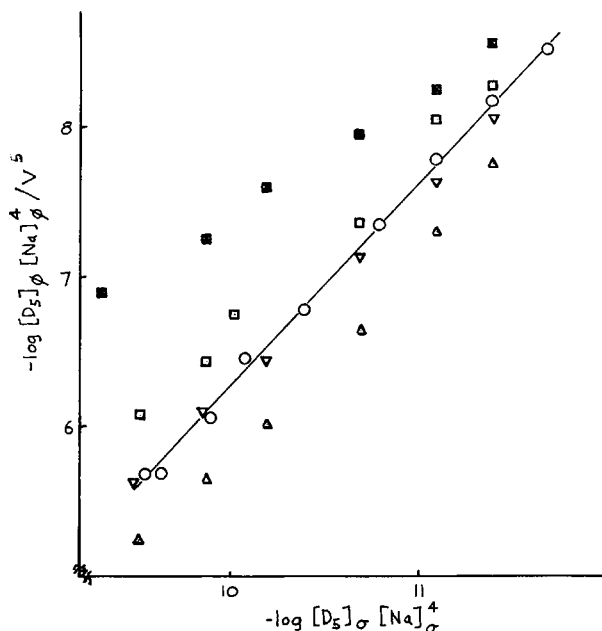


Fig. 7. Equilibrium adsorption of Sky Blue 6B at 90°C: (O) single dyeing; (■) mixture with D₁, 1:1; (Δ) D₂; (□) D₃; (▽) D₄; NaCl concentration, 0.03 mole/l.

surface in substrate. Factor (1) is capable of numerical treatment by eq. (3), and factor (2), by eq. (8).

Factor (3) mainly contributes to equilibrium conditions in mixtures of Chrysophenine G and Sky Blue 6B, and is described by the method of Horiki et al.,^{8,10} Daruwalla et al.,¹⁸ and Morita et al.¹⁹ Therefore, if the activity coefficient of all ionic species in the fiber and dye bath phase is unity (or nearly equal to unity), the adsorption behavior in mixture dyeing may well be described by eqs. (3) and (8).

The standard affinity in mixture dyeing ($-\Delta\mu_{D_i}^0$) at 70° and 90°C was calculated by eqs. (3) and (8), which is shown in Tables III–X, and was nearly equal to that in single dyeing except for the mixture of Chrysophenine G and Sky Blue 6B. The same additivity of standard affinity as that of the acid dyeing of nylon²⁰ was verified.

Therefore, in binary mixture dyeing of direct dyes, except for the mixture of Chrysophenine G and Sky Blue 6B, factors (1) and (2) play a predominant role, and factor (3) is not involved. Earlier investigation also suggested that factor (3) or complex formation in the dye bath was involved, especially in the Chrysophenine G–Sky Blue 6B system.^{8,10,11} Because Neale and Stringfellow¹⁰ and Horiki et al.¹¹ gave special attention to the system, they emphasized the importance of factor (3).

In the above discussion, it was assumed that there was additivity of standard affinity in mixture dyeing. However, fiber and solution log sum plots of each dye in single and mixture adsorption, based on eqs. (1), (2),

TABLE XI
Equilibrium Adsorption of D_1 and D_2 in Single and Mixture Dyeings^a

	$[D_1]_{\sigma}$ mole/l.	$[D_1]_{\phi}$ mole/l.	$[D_2]_{\phi}$ mole/kg	$[D_2]_{\phi}$ mole/kg	$[D_1]_{\sigma} + [D_2]_{\sigma}$ mole/l.	$[D_1]_{\phi} + [D_2]_{\phi}$ mole/kg	$[Na]_{\sigma}$ mole/l.	$[Na]_{\phi}$ mole/kg
Mixture dyeing	1.99×10^{-6}	8.43×10^{-6}	3.64×10^{-4}	1.03×10^{-2}	2.83×10^{-6}	1.07×10^{-2}	3.01×10^{-2}	2.78×10^{-2}
Single dyeing	1.99×10^{-6}	8.47×10^{-6}	1.02×10^{-3}	1.06×10^{-2}	1.99×10^{-6}	1.02×10^{-3}	3.00×10^{-2}	1.46×10^{-2}
					8.47×10^{-6}	1.06×10^{-2}	3.00×10^{-2}	2.78×10^{-2}

^a At 90°C, NaCl concentration 0.03 mole/l.

(3), and (8), shows the same slope and a small but definite difference in intercept (Figs. 3-7). It follows that there is no strict additivity of standard affinity. This difference in intercept will be discussed below.

The adsorption of a dye in admixture is different from single adsorption in that a second dye in the system and an increase in sodium ion is introduced by the second dye. The adsorption of Chrysophenine G and Benzopurpurine 4B, for instance, was as shown in Table XI. (Data were selected from Table III and from the corresponding single dyeing, and the concentration of Na ion was added.) The adsorption of Chrysophenine G decreased to half of single adsorption when Benzopurpurine 4B at half the concentration of Chrysophenine G was added. The total adsorption $[D_1]_f + [D_2]_f$ became ten times that of $[D_1]_f$ in single dyeing. While the total dyebath concentration was one and a half that of single adsorption and $[Na]_s$ was constant, $[Na]_f$ doubled. The difference in intercept mentioned above is attributable to these changes, because the activity coefficient of Chrysophenine G on the fiber became smaller by a tenfold increase in total adsorption in spite of the adsorption decrease. Though the increase in $[Na]_s$ was twofold, a similar effect was produced by the increase in total adsorption. It follows that the higher the standard affinity of the second dye in the mixture combination with Chrysophenine G, the larger the difference in intercept.

On the other hand, in the adsorption of Benzopurpurine 4B no deviation was found in intercept within the experimental error (Fig. 4). Similar comparison of single and mixture adsorption as in the case of Chrysophenine G shows a change in total dyebath concentration $[D_1]_s + [D_2]_s$, about a threefold increase in $[D_2]_s$ in single dyeing. These changes in dyebath concentration were considered to bring about no appreciable change in activity coefficient. Consequently, Benzopurpurine 4B may show no deviation in intercept. In the fiber and solution log sum plots of Figures 3-7, Benzopurpurine shows least deviation in intercept, i.e., least effect given by the second dye. The position of these log sum plots in mixture adsorption is in the following order: Sirius Red 4B \approx Chrysophenine G > Sirius Supra Blue BRR \approx Sky Blue 6B > Benzopurpurine 4B. In the Chrysophenine G and Sirius Red 4B system, there was no difference in the plots between the 1:1 and 2:1 mixtures. It follows that such changes in mixture ratio give no deviation in log sum plot or in activity coefficient.

These facts, in general, show that the deviation in intercept of the log sum plot, or a small difference between $\Delta\mu_i^0$ and $\Delta\mu_{D_i}^0$, may be produced mainly by the effect of the change in total adsorption on fiber on the activity coefficient of dye anion and sodium ion.

The above discussions about the differences in the slope and intercept of log sum plots appear to show that a substrate model whose internal volume is constant is a reasonable assumption.

With adsorptions at 70°C, there was no difference in adsorption behavior from that at 90°C; consequently, the same conclusion as at 90°C has been reached.

Thus, mixture dyeing of direct dyes, except for the Chrysophenine G and Sky Blue 6B system where complex was formed in the dye bath, can be treated as a monomolecularly diffuse adsorption model, as in single dyeing.

In the diffusion of direct dyes in admixture, even non-Fickian diffusion was found.²¹ Although the apparent diffusion coefficient of each dye became larger than that in single dyeing, whose surface concentration was similar to that in mixture dyeing, the dye of larger affinity had a more profound effect on the diffusion of the dye of smaller affinity than in the reverse case. This phenomena is attributed to a competition of available surfaces in the substrate, which is well described by eqs. (3) and (8) in the case of mixture adsorption.

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