Studies on Mixture Dyeing. III.[1] The Absorption Spectra of Direct Dye Mixtures in an Aqueous Solution

By Zenzo MORITA and Minoru SEKIDO

(Received December 22, 1964)

Since Neale and Stringfellow[2] discovered that most of the binary mixtures of dyes in an aqeous solution showed non-additive spectra, the interaction between molecules of different kinds of dyes in an aqueous solution has been studied extensively.[3-10]

Derbyshire and Peters[3] have investigated the interaction between Chrysophenine G and Sky Blue FF, for which pair Neale and Stringfellow[2] found the strongest interaction in an aqueous solution, measured the heat of the formation of the 1:1 complex of the two dyes to be -15 kcal./mol. by direct colorimetry, and concluded that the formation of the 1:1 complex occurred in an aqueous solution to an appreciable extent, even at 90°C.

Tanizaki, Kobayashi and Ando[4] have confirmed the non-additivity of the absorption spectra of a binary mixture with Sky Blue FF in an aqueous solution. Kobayshi Tanizaki and Ando,[5-7] and Kobayshi, Saito, Tanizaki and Ando[8] obtained the equilibrium constants for a 1:1 complex with many kind of two dyes. Inscore, Gould, Corning and Brode[9] observed the absorption spectra of binary dye mixtures in an aqueous solution and discussed qualitatively the relation between the structure of these dyes and the strength of the interaction between them. Very recently, Hoshi[10] has investigated spectroscopically the interaction in an aqueous solution between Chrysophenine G and the blue dyes derived from dianisidine as diazo components.

The investigations above quoted,[3-8,10] however, have some limitations in terms of the chemical structure of dyes. For the present paper, therefore, five typical dyes (cf. Table I) were selected in order to extend the scope of the study of the interaction, this study revealed that the interaction of Chrysophenine G and Sky Blue 6B is very strong and that the absorption spectra of the mixture of Chrysophenine G and Sirius Supra Blue BRR are almost additive.[2] Sirius Red 4B and Sirius Supra Blue BRR are typical unsymmetrical, direct dyes, and in terms of dyeability the other three dyes have been investigated as typical models of direct dyes. These five dyes may, then, be assumed to be representative so far as their shape, structure, dyeability, and molecular weight are concerned. In view of the above-mentioned reasons, the study of the interaction between every two of these five dyes would be helpful in obtaining a general idea of the combinations of most direct dyes commercially available.

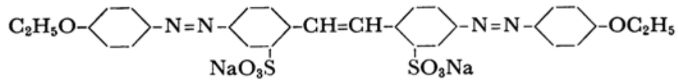
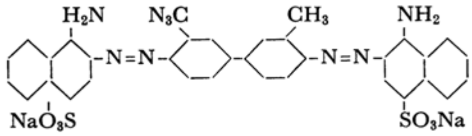
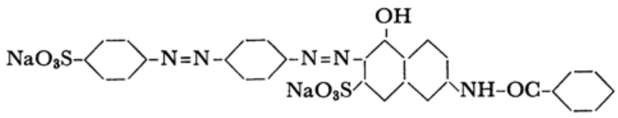
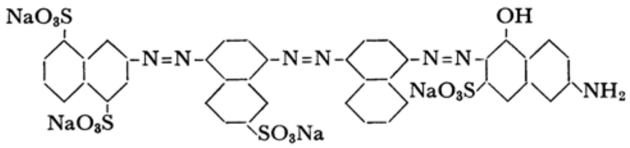
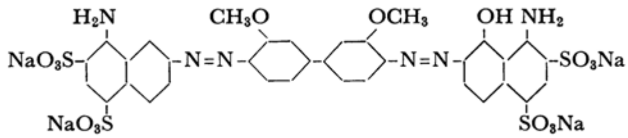
In the present paper the equilibrium constants for the complexes of six combinations among the ten will be obtained spectroscopically at room temperature. Because of the overlapping of their absorption spectra, the equilibrium constants of the other combinations were unobtainable.

Experimental

Purified dyes were used throughout. The samples of Chrysophenine G, Benzopurpurine 4B, Sirius Red 4B and Sky Blue 6B were the same as those used before.[1,11]

1) Part II: M. Sekido and Z. Morita, This Bulletin, **36**, 1602 (1963).
2) S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Colourists*, **59**, 241 (1943).
3) A. N. Derbyshire and R. H. Peters, ibid., **72**, 268 (1956).
4) Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1956).
5) T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **32**, 675 (1959).
6) T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **32**, 680 (1959).
7) T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **33**, 661 (1960).
8) T. Kobayashi, K. Saito, Y. Tanizaki and N. Ando, ibid., **35**, 935 (1962).
9) M. N. Inscore, J. H. Gould, M. E. Corning and W. R. Brode, *J. Res. Natl. Bur. of Std.*, **60**, 65 (1958).
10) T. Hoshi, Master's Dissertation, Tokyo Institute of Technology (1963).
11) M. Sekido and Z. Morita, This Bulletin, **35**, 1375 (1962).

TABLE I. DYE STRUCTURES

Name (C. I. Direct No.)	Structure
Chrysophenine G (Yellow 12)	
Benzopurpurine 4B (Red 2)	
Sirius Red 4B* (Red 81)	
Sirius Supra Blue BRR* (Blue 71)	
Sky Blue 6B (Blue 1)	

* Although Chlorazol Fast Red K and Chlorazol Fast Blue 2BN, used by Neale and Stringfellow,[2] are not listed in "Colour Index 2nd ed.," they are similar to Sirius Red 4B and Sirius Supra Blue BRR, respectively by "Colour Index 1 st ed." and "Schultz's Farbstofftabellen 7 th ed."

Sirius Supra Blue BRR were purified from commercial dyes (Sumilight Supra Blue BRR (NSK)) by the method of Robinson and Mills.[12] The absence of colored impurities was checked by paper chromatography.

All the concentrations were determined by weight. All of the absorption spectra were mesured in a 1.0 cm. cell by a Hitachi EPB-V type spectrophotometer at room temperature.

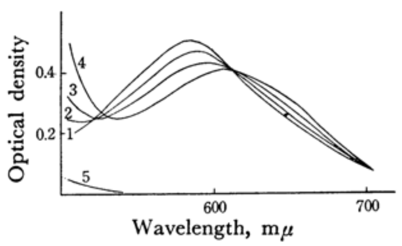


Fig. 1. Absorption spectra of the mixture of Chrysophenine G and Sirius Supra Blue BRR in aqueous solution at 16°C.

	Sirius Supra Blue BRR	Chrysophenine G, mol./l.
1	$6.57_6\times10^{-6}$	0
2	$6.57_6\times10^{-6}$	$6.40_8\times10^{-6}$
3	$6.57_6\times10^{-6}$	13.2_0
4	$6.57_6\times10^{-6}$	29.4_2
5	0	10.0_0 (calculated from molar extinction coefficient)

Results and Discussion

The absorption spectra of two combinations among the six investigated are shown in Figs. 1 (Chrysophenine G - Sirius Supra Blue BRR) and 2 (Benzopurpurine 4B - Sky Blue 6B). These spectra show the same non-additivity as those early investigated,[2-9] but when the concentration of a component increases, no second isosbestic point, which corresponds to the formation of a 1:2 complex, is found.[7,10] It follows that only a 1:1 complex is formed in all the concentrations. Though the absorption spectra of the mixtures of Chrysophenine G and Sirius Supra Blue BRR were found to be almost additive by Neale and Stringfellow,[2] Fig. 2 shows the non-additive spectra and the presence of an isosbestic point.

In the determination of the equilibrium constants from spectroscopic measurements, the method of Benesi and Hildebrand[13] and modifications of it[14-16] have been most commonly employed. Some other methods have been proposed for the

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

13) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

14) V. J. A. Ketelaar, C. von de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

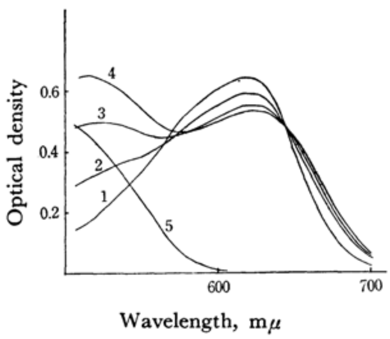


Fig. 2. Absorption spectra of the mixture of Benzopurpurine 4B and Sky Blue 6B in aqueous solution at 18°C.

	Sky Blue 6B	Benzopurpurine, 4B mol./l.
1	$6.46_8\times10^{-6}$	0
2	$6.46_8\times10^{-6}$	$2.41_2\times10^{-6}$
3	$6.46_8\times10_{-}{}^{6}$	5.97_1
4	$6.46_8\times10^{-6}$	11.2_8
5	0	10.0_0 (calculated from molar extinction coefficient)

determination of the equilibrium constants of dye-dye complexes.[5,10,17] In this paper Nash's method,[18] which permits a direct evaluation of the equilibrium constant with a minimum of computational labor, has been used.

Following Nash's presentation, it is assumed that there are chemical equilibria of the forms:

$$S + D = SD \tag{1}$$

$$SD + D = SD_2 \tag{2}$$

where D is any donor dye molecule; S, an acceptor substrate and SD and SD_2, 1:1 and 1:2 complexes respectively. The equilibrium constants appropriate to reactions 1 and 2 are given in concentration units by:

$$K_1=\frac{C_{SD}}{C_S\cdot C_D} \tag{3}$$

$$K_2=\frac{C_{SD2}}{C_{SD}\cdot C_D} \tag{4}$$

where C_{SD} and C_{SD_2} are the equilibrium concentrations of SD and SD_2, and C_S and C_D are the final concentrations of S and D respectively.

In order to obtain the equilibrium constant of the complex between the S and D dyes, the spectroscopic measurement of mixture solutions containing a constant concentration of the S dye and various concentrations of the D dye is required. $A°$ denotes the optical density at a wavelength when the concentration of the D dye is zero, while A denotes the optical density of the mixture solution when the final concentration of the D dye is C_D. When the reciprocal of the donor dye concentration is plotted against the reciprocal of (one minus the absorbance ratio) (i. e., $1/C_D$ vs. $A°/(A°-A)$), a straight line results if a 1 : 1 complex is formed. The intercept of this line is equal to the negative of the equilibrium constant.

However, it is necessary that the absorbance of the D dye at the wavelength be zero, and that the difference between $A°$ and A be as large as possible. With these points in mind, the wavelength of 680 mμ was used. The results are shown in Figs. 3

Table II. Equilibrium constants for the complex between dyes

Dye (1)	Dye (2)	K_1 l./mol.	Temp. °C
Sky Blue 6B	Chrysophenine G	1.7×10^7	18
	Benzopurpurine 4B	1.8×10^5	18
	Sirius Red 4B	5.0×10^4	18
Sirius Supra Blue BRR	Chrysophenine G	ca. 1.0×10^4	16
	Benzopurpurine 4B	5.0×10^4	16
	Sirius Red 4B	1.4×10^5	16

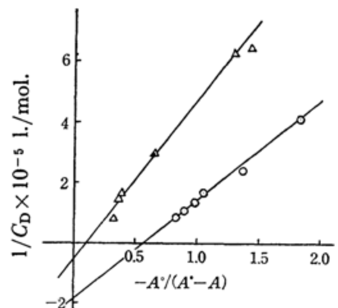


Fig. 3. The interaction of Sky Blue 6B with Benzopurpurine 4B (○) and Sirius Red 4B (△). The concn. of Sky Blue 6B=$6.46_8\times10^{-6}$ mol./l.; 680 mμ

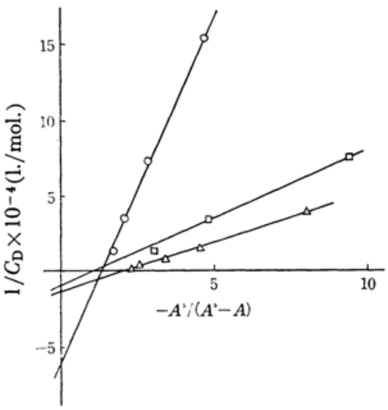


Fig. 4. The interaction of Sirius Supra Blue BRR with Chrysophenine G (□), Benzopurpurine 4B (○) and Sirius Red 4B (△).
The concn. of Sirius Supra Blue BRR=$6.57_6\times10^{-6}$ mol./l.; 680 mμ

15) R. L. Scott, ibid., **75**, 787 (1956).
16) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **74**, 1891 (1952).
17) D. R. Lemin and T. Vickerstaff, *Trans. Faraday Soc.*, **43**, 491 (1947).
18) C. P. Nash, *J. Phys. Chem.*, **64**, 950 (1960).

and 4, while the equilibrium constant, K_1 is given in Table II. When the other wavelength was used, similar results were obtained.

The equilibrium constant for the complex of Chrysophenine G and Sky Blue 6B, as determined by Kobayashi, Tanizaki and Ando,[7] is different from that as determined by Hoshi;[10] this is due to the dissimilar concentrations of Sky Blue 6B. The absorption spectra of the mixture of Chrysophenine G and Sky Blue 6B are shown in Fig. 5. In this case, the equilibrium constant for the 1 : 1 complex could not be calculated by Nash's method because of the smaller concentration of Chrysophenine G (D) than of Sky Blue 6B (S), against the assumption $S \ll D$. Moreover, the equilibrium constants, K_1 and K_2, can be calculated by the method using the two isosbestic points corresponding to formations of 1 : 1 and 1 : 2 complexes.[10] The evaluation of the molar extinction coefficient of the SD_2 complex at the wavelength of the first isosbestic point is not easy by this method. At this wavelength, however, K_2 can be obtained with ease by Nash's method (Fig. 6). Here A° for Eq. 2 (the optical density of SD when the concentration of dye D is zero) corresponds to the first isosbestic point. K_1 and K_2 are $1.7_4 \times 10^7$ and $4.2_5 \times 10^5$ respectively, and they are in the range of values investigated earlier.[7,10]

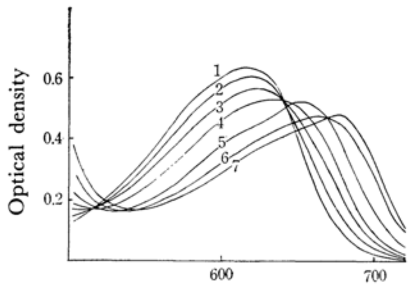


Fig. 5. Absorption spectra of the mixture of Chrysophenine G and Sky Blue 6B in aqueous solution at 18°C.

	Sky Blue 6B	Chrysophenine G, mol./l.
1	$6.46_8 \times 10^{-6}$	0
2	$6.46_8 \times 10^{-6}$	$1.22_7 \times 10^{-6}$
3	$6.46_8 \times 10^{-6}$	2.69_0
4	$6.46_8 \times 10^{-6}$	4.38_7
5	$6.46_8 \times 10^{-6}$	8.60_2
6	$6.46_8 \times 10^{-6}$	18.6_6
7	$6.46_8 \times 10^{-6}$	36.7_9

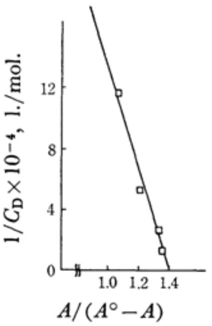


Fig. 6. The interaction of Sky Blue 6B with Chrysophenine G.
The concn. of Sky Blue 6B$=6.46_8 \times 10^{-6}$ mol./l.; 640 mμ

The K_1 values for Chrysophenine G and Sky Blue 6B complexes are extremely large compared with those in Table II while the K_1 values for Chrysophenine G and Sirius Supra Blue BRR complexes are small. This can be supposed on the basis of the results reported earlier.[2] The strength of the interaction is of the following order: Chrysophenine G - Sky Blue 6B > Benzopurpurine 4B - Sky Blue 6B > Sirius Red 4B - Sirius Supra Blue BRR > Sirius Red 4B - Sky Blue 6B = Benzopurpurine 4B - Sirius Supra Blue BRR > Chrysophenine G - Sirius Supra Blue BRR. It follows that the combination of Chrysophenine G and Sky Blue 6B is a typical one in direct dyes, and that the equilibrium constants for dye-dye complexes in an aqueous solution at room temperature are in the 10^7—10^4 range. The order of the magnitude of K_1 may confirm the qualitative observations by Inscore, Gould, Corning and Brode.[9]

Some factors influencing the interaction between dyes have been studied. The exact nature of the forces operative in the interaction and the manner how these dyes form complex have not yet been determined. However, since it is clear that the interaction between unlike dye molecules is stronger than that between like molecules, the aggregation of like dye molecules is less favorable than the complex formation between unlike molecules, such as Chrysophenine G and Sirius Supra Blue BRR. It follows that the equilibrium constant for a complex between like dye molecules is very much smaller than 10^4.

Summary

The absorption spectra of a binary mixture of five representative direct dyes in solution have been investigated. The equilibrium constants for complex formation are in the 10^7—10^4 range and are in the order: Chrysophenine G - Sky Blue 6B > Benzopurpurine 4B - Sky Blue 6B > Sirius Red 4B - Sirius Supra Blue BRR > Sirius Red 4B - Sky Blue 6B = Benzopurpurine 4B - Sirius Supra Blue BRR > Chrysophenine G - Sirius Supra Blue BRR. The combination of Chrysophenine G and Sky Blue 6B is a typical one in direct dyes. The equilibrium constant for an aggregation of like dye molecules is very much smaller than the value of 10^4 at room temperature.

Division of Polymer Science
Tokyo Institute of Technology
Ookayama, Tokyo