The Adsorption of Dye Mixtures by Cellophane Sheet. I. Temperature and Concentration Dependence of Adsorption from Some Binary Mixtures

By Yukio HORIKI, Yoshié TANIZAKI and Noboru ANDO

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It is well known that the amount of adsorption of dyes from binary mixtures of a direct dye with others is commonly reduced as compared with the adsorbed dye amount when dyed singly[1-3]. Some factors of such reduction of adsorption in mixture dyeing have been variously discussed, and it seems to be most appropriate to consider a mutual interaction between dyes in solution as a principal factor. Neale and Stringfellow have considered that such interaction is attributed to the complex formation[2]. This concept, however, has failed to be accepted, because there is no direct evidence of complex formation in solution at such a high temperature as is practically applied[4]. Derbyshire and Peters[3] have recently shown by the spectroscopic measurements that Chlorazol Sky Blue FF and Chrysophenine G form a 1 : 1 complex in aqueous solution containing no salt at 60°C, and further concluded by the thermodynamic treatment that the complex formation occurs even at a usual dyeing temperature 90°C. Based on this conclusion, they have discussed in a semi-quantitative way the results of mixture dyeing.

In the hope of finding a method to obtain some quantitative information about the interaction between dyes in mixture dyebath, necessary to explain the reduction in adsorption, the authors have studied the single and the mixture dyeings of Chlorazol Sky Blue FF and Chrysophenine G, and of Chlorazol Sky Blue FF and a monoazo acid dye.

Experimental

Chlorazol Sky Blue FF and Chrysophenine G were used as direct dyes, and *p*-nitroaniline→γ acid (α-coupling) as a monoazo acid dye. Chlorazol Sky Blue FF (called Blue dye for short) and the monoazo acid dye (Acid dye) were the same as those used in the authors' previous works[5,6], and Chrysophenine G (Yellow dye) was prepared by purifing the commercial dye by Robinson and Mills' method[7].

The Cellophane sheet used was that made by Tokyo Cellophane Co., Ltd. It was washed with distilled water at 90°C for 30 min. Pieces of the sheet weighing 15~25 mg. were dyed in 75 g. portions of the dye solution at 50, 70 and 90°C for 24 hr.* The dyed sheets were rinsed in ice-cold water (about 6°C) and then left in a desiccator with 50% sulfuric acid for two days. An accurate weight of the dyed sheet was obtained by dividing its weight under the constant humidity by a known humidity coefficent (e. g. 1.07 at 15°C and 1.10 at 30°C)[8].

Check measurements on solutions of known density in 25% aqueous pyridine showed that the dyes obeyed Beer's law both singly and in mixture, and that the absorption spectra in the mixture were additive. Based on this fact, the dye adsorbed by the sheet was stripped with 25% aqueous pyridine and the dye content of the strip solution was measured by a Shimadzu QR-50 spectrophotometer.

In case of the mixture dyeing, the initial concentration of Blue dye was about 1×10^{-5} mol./l. for every dyebath, and those of Yellow dye and Acid dye were varied from zero to about 35×10^{-5} and 90×10^{-5} mol./l., respectively. The concentration of sodium chloride was 2.0 g./l. for every dyebath.

Results

The relation between the amount of adsorption of Blue dye and the dyebath concentration of its partners was examined, 24 hr. after mixture dyeing, by the

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[1] J. Boulton, A. E. Delth, F. Forthergrill and T. H. Morton, *J. Textile Inst.*, **24**, 113 (1933).

[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] T. Vickerstaff, "The Physical Chemistry of Dyeing", 2nd Ed., Oliver & Boyd, London (1954), p. 242.

[5] Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1954).

[6] T. Kobayashi, Y. Tanizaki and N. Ando, ibid., **32**, 675 (1959).

[7] C. Robinson and H. A. T. Mills, *Proc. Roy. Soc.* (*London*), **A131**, 576 (1931).

[8] K. Nishida, *J. Soc. Textile Cellulose Ind. Japan* (*Sen-i Gakkaishi*), **7**, 539 (1951).

* This time of of dyeing (24 hr.) may be enough for only a qualitative discussion of the behavior of mixture dyeing.

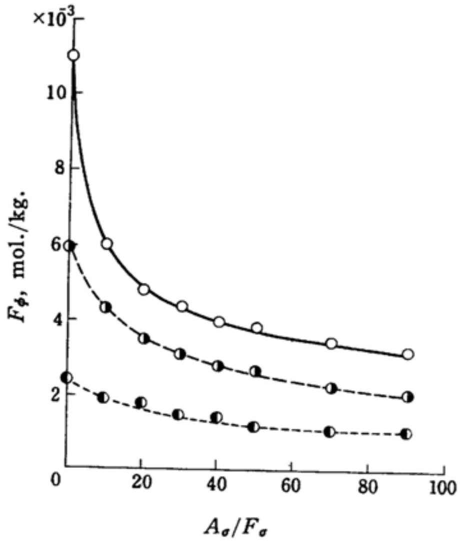

Fig. 1. The relation between the adsorption of Blue dye (F_ϕ) from a mixture dyebath with Acid dye and the ratio of final dyebath concentration of Acid dye (A_σ) to that of Blue dye (F_σ).

—○— 50°C, --◑-- 70°C, ---◐--- 90°C

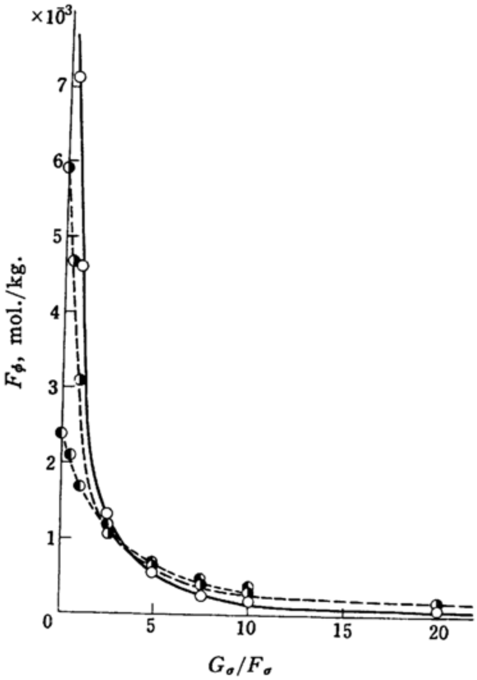

Fig. 2. The relation between the adsorption of Blue dye (F_ϕ) from mixture dyebath with Yellow dye and the ratio of final dyebath concentration of Yellow dye (G_σ) to that of Blue dye (F_σ).

—○— 50°C, --◑-- 70°C, ---◐--- 90°C

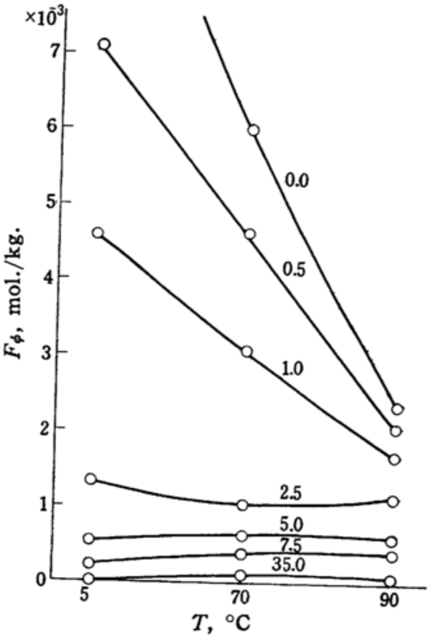

Fig. 3. Effect of temperature on the adsorption of Blue dye from mixture dyebath. The numbers indicate the ratio of the initial dyebath concentration of Yellow dye to that of Blue dye.

adsorption measurements of binary mixtures containing a constant amount of Blue dye. The results are shown in Figs. 1 and 2; the one denotes the pair of Blue dye and Acid dye, and the other Blue dye and Yellow dye. Comparison between these figures shows that the adsorption of Blue dye is not so decreased with an increase in the dyebath concentration of Acid dye (Fig. 1), while it is markedly reduced by the addition of a very small amount of Yellow dye until it rapidly converges to zero (Fig. 2). Furthermore, under the present condition, the adsorption of Blue dye from a dyebath, containing several times as much Yellow dye as Blue dye, slightly increases with a raise in temperature; this is the same tendency as that reported by Neale and Stringfellow2). This situation can be recognized by the relation between the adsorption of Blue dye and temperature in Fig. 3.

In case of mixture dyeing with Blue dye the adsorption of the partner, i. e. Yellow dye or Acid dye, is also reduced, as compared with that in the case of its single dyeing. For instance, adsorption curves of Yellow dye from single and mixture dyebaths at 70°C, corresponding to Fig. 2, are shown in Fig. 4a.

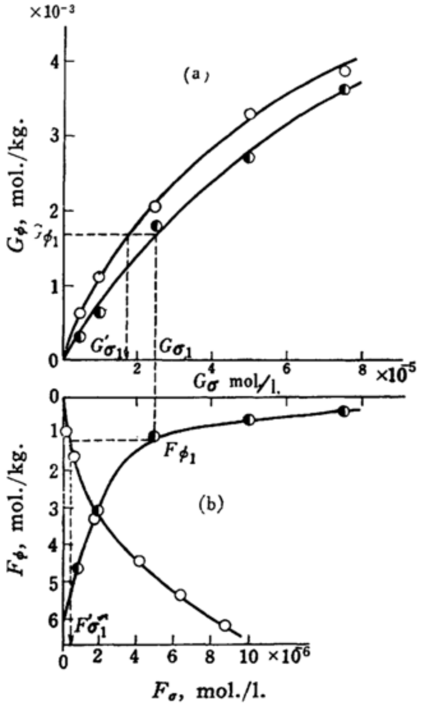

Fig. 4. The adsorptions of Blue dye and Yellow dye from single and mixture dyebaths at 70°C. Here the results of mixture dyeing correspond to those of Fig. 2. Scale (F_σ) on the abscissa (b) refers to the white circles.
○ Single ◐ Mixture

It has been seen that the affinity of Blue dye**, obtained from its single dyeing (corresponding to the white circles in Fig. 4b), is more or less dependent on its dyebath concentration at constant temperature. The relation between the affinity of Blue dye and its final dye bath concentration at various temperatures in single dyeing is shown in Fig. 5. This figure shows that the affinity, $-\Delta\mu^0$, is approximately proportional to the logarithm of the final dyebath concentration of Blue dye, F_σ. In this figure is also shown the relation between $\log F_\sigma$ and the concentration of sodium ion in Cellophane, Na_ϕ**.

Discussion

Based on the assumption that the reduction of the amount of dyes resulting from the mixture dyeing is due to an interaction between the two dyes, the results described in the preceding section will be discussed. Now, let us assume simply that:

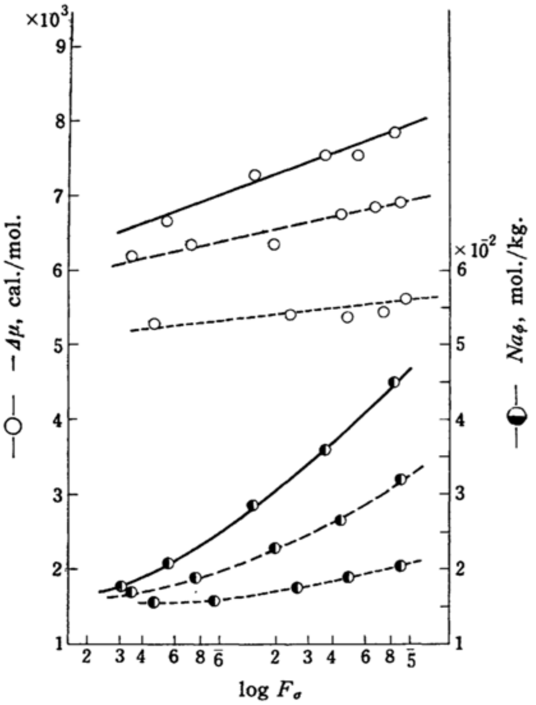

Fig. 5. The relations of the affinity ($-\Delta\mu^0$) of Blue dye for Cellophane (white circles) and of the concentration of sodium ion (Na_ϕ) in Cellophane (half solid circles) to the logarithm of final dyebath concentration of Blue dye (F_σ, mol./l.).
—— 50°C, ---- 70°C, ------ 90°C

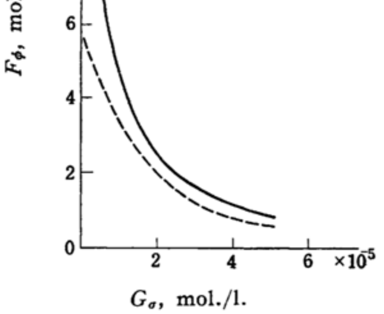

Fig. 6. The relation between the dyebath concentration of Yellow dye and the adsorption of Blue dye calculated from Eqs. 1 and 3. $F_\sigma=1\times10^{-5}$ mol./l., $K_{50°}=6\times10^{-7}$ mol./l., $K_{70°}=1\times10^{-6}$ mol./l.
—— 50°C, ---- 70°C

** $Na\phi$ and $-\Delta\mu^0$ were calculated from Eqs. 7.19 (p. 200) and 7.26 (p. 206) in Ref. 4. V (surface layer volume) =0.45 l./kg. for each dyeing temperature.

1) The effective dyebath concentration which contributes to adsorption is reduced by an interaction between both dyes in mixture.

2) The amount of the dye adsorbed from the mixture dyebath corresponds to this effective dyebath concentration, and the adsorbing behavior of the dye in mixture dyeing is just the same as that in its single dyeing, so it behaves independently. Consequently, concerning the effective dyebath concentration, the additivity in adsorption comes into being.

These assumptions may be appropriate under the condition that no competition of dyes for the available surface occurs. If the assumptions are accepted, the effective dye bath concentration will be calculated by the following equation, using the amount of dye adsorbed from mixture dyeing and its affinity obtained from single dyeing,

$$D_\phi = Na_\phi^{-z} Na_\sigma^{+z} V^{z+1} D_\sigma' \exp(-\Delta\mu^0/\boldsymbol{R}T) \tag{1}$$

where D_ϕ (mol./kg.) is the amount of a dye adsorbed by Cellophane, D_σ' (mol./l.) the effective dyebath concentration, Na_ϕ (mol./kg.) the sodium ion concentration in Cellophane, Na_σ (mol./l.) the sodium ion concentration in dyebath, V (l./kg.) the surface layer volume, $-\Delta\mu^0$ (cal./mol.) the standard affinity, $\boldsymbol{R}$ and T the gas constant and the absolute temperature, respectively, and z the number of sulfonic groups per molecule. The difference D_c (mol./l.) between the total dyebath concentration D_σ (mol./l.) and the effective dyebath concentration may be attributed to the interaction of dyes in mixture solution; in other words, D_c may be regarded as the dyebath concentration ineffective to adsorption. If the amount of a dye adsorbed in this mixture dyeing is known, it would be expected that its effective dyebath concentration would be calculated by Eq. 1. However, as the calculated affinity of dyes generally varies more or less with the dyebath concentration, it is undesirable to calculate it directly by Eq. 1. Therefore, it was obtained graphically from the observed values in single and mixture dyeings. Concerning the pair of Blue dye and Yellow dye, for example, its effective dyebath concentration is obtained from Figs. 4a and 4b as follows: when the final total dye bath concentrations of Blue dye and Yellow dye are $F_{\sigma 1}$ and $G_{\sigma 1}$, respectively***, as shown in the figure, the amounts of adsorption of the dyes $F_{\phi 1}$, $G_{\phi 1}$ correspond to $F_{\sigma 1}'$, $G_{\sigma 1}'$ in single dyeing, respectively, which may be regarded as their effective dyebath concentrations. $F_{\sigma 1}-F_{\sigma 1}' \equiv F_{c1}$ and $G_{\sigma 1}-G_{\sigma 1}' \equiv G_{c1}$ may be regarded as the concentrations participated in the interaction, and it follows that G_{c1}/F_{c1} means the mole ratio of both dyes contributed to the interaction. Values obtained in such a way are shown in Tables I and II. Table I shows that G_c/F_c tends to about unity when the relative concentration of Yellow dye to Blue dye increases to a certain value. If it is assumed that the interaction in this range of concentration means the formation of a 1:1 complex, it is possible to calculate the instability constant K of the complex, according to the mass action law,

$$K = \frac{F_\sigma' G_\sigma'}{F_c} = \frac{(F_\sigma - F_c)(G_\sigma - G_c)}{F_c}, \quad (F_c = G_c) \tag{2}$$

Values of K calculated by the equation are shown in Table I.

When the value of K is known, the effective dyebath concentration will be obtained from Eq. 2. For example, F_σ' can be given as a function of F_σ and G_σ, by the following equation which was derived from Eq. 2,

$$F_\sigma' = F_\sigma - F_c = \frac{1}{2}\{(G_\sigma - a)^2 + (b^2 - a^2)\}^{1/2} + \frac{1}{2}(a - G_\sigma) \tag{3}$$

where $a = F_\sigma - K$ and $b = F_\sigma + K$. Since a and b are constant when F_σ is fixed, F_σ' is the function of G_σ alone. Further, the value of F_ϕ in the mixture of Blue dye and Yellow dye can be obtained by substituting F_σ' into Eq. 1.

In order to check the validity of the assumption described above, values of F_σ' corresponding to various values of G_σ were calculated by Eq. 3; here were used 6×10^{-7} and 1×10^{-6} mol./l. as the values of K_{50° and K_{70°, respectively, and 1×10^{-5} mol./l. as that of F_σ and $0.5\times10^{-5} \sim 5\times10^{-5}$ mol./l. as that of G_σ. The values of F_ϕ are also calculated by Eq. 1, using the obtained values of F_σ', where Na_ϕ and $-\Delta\mu^0$ were obtained graphically from Fig. 5, and 3.42×10^{-2} mol./l. and 0.45 l./kg. were used as the values of Na_σ and V, respectively. These calculated values of F_ϕ against

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*** Since the total concentration of Blue dye is nearly constant (1×10^{-5} mol./l.), $G_{\sigma_1}/F_{\sigma_1}$ is dependent only on G_{σ_1}. Suffix 1 denotes some fixed values of F_σ, G_σ, etc.

TABLE I. RESULTS OF MIXTURE DYEING OF BLUE DYE AND YELLOW DYE

T°C	F_σ $\times 10^6$ mol./l.	F_ϕ $\times 10^3$ mol./kg.	F_σ' $\times 10^6$ mol./l.	F_c $\times 10^6$ mol./l.	G_c/F_c	K, mol./l.	G_c $\times 10^6$ mol./l.	G_σ' $\times 10^6$ mol./l.	G_ϕ $\times 10^3$ mol./kg.	G_σ $\times 10^6$ mol./l.
50	8.04	7.1	3.2	4.8	0.7	—	3.3	1.5	0.6	4.83
	8.88	4.6	1.3	7.6	0.7	—	5.1	4.6	1.3	9.70
	9.75	1.3	0.4	9.4	1.2	4.7×10^{-7}	11.0	14.0	2.8	24.5
	9.87	0.6	0.2	9.7	1.2	7.4×10^{-7}	12.0	37.0	5.2	48.8
70	8.59	4.6	4.6	4.0	0.7	—	2.6	2.3	0.3	4.89
	9.39	3.1	2.1	7.3	0.5	—	3.6	6.3	0.6	9.87
	9.73	1.1	0.4	9.3	0.5	—	4.6	20.0	1.8	24.6
	9.86	0.6	0.3	9.6	1.3	9.6×10^{-7}	12.0	37.0	2.7	49.4
90	9.90	0.4	0.9	9.0	0.9	7.4×10^{-6}	8.0	70.0	1.7	78.0
	9.96	0.2	0.7	9.3	1.0	1.4×10^{-5}	9.0	190.0	3.5	199.0

Notations, F_σ etc. and G_σ etc., refer to Blue dye and Yellow dye, respectively.
K means the instability constant of complex. $(F_c+G_c)/2$ was regarded as the concentration of complex in the range $0.9\leqq G_c/F_c\leqq 1.3$.

TABLE II. RESULTS OF MIXTURE DYEING OF BLUE DYE AND ACID DYE

T°C	F_σ $\times 10^6$ mol./l.	F_ϕ $\times 10^3$ mol./kg.	F_σ' $\times 10^6$ mol./l.	F_c $\times 10^6$ mol./l.	A_c/F_c	A_c $\times 10^6$ mol./l.	A_σ' $\times 10^5$ mol./l.	A_ϕ $\times 10^3$ mol./kg.	A_σ $\times 10^4$ mol./l.
50	8.98	4.9	1.4	7.6	1.1	8	1.2	1.6	2.0
	8.96	4.4	1.2	7.8	1.2	9	2.1	2.2	3.0
	9.14	4.0	1.0	8.1	1.4	11	2.9	2.6	4.0
	9.15	3.5	0.9	8.3	1.4	28	4.2	3.2	7.0
70	9.25	3.1	2.0	7.3	2.3	17	1.3	1.5	3.0
	9.36	2.8	1.7	7.7	2.7	21	1.9	1.8	4.0
	9.47	2.3	1.2	8.3	3.3	27	4.3	2.6	7.0
	9.55	2.1	1.1	8.5	3.4	29	6.1	3.1	9.0
90	9.61	1.8	5.4	4.2	1.9	8	1.2	0.8	2.0
	9.67	1.4	3.7	6.0	2.4	14	2.6	1.3	4.0
	9.73	1.3	3.1	6.6	3.0	20	3.0	1.5	5.0
	9.73	1.1	2.5	7.2	3.3	24	4.6	1.9	7.0
	9.76	1.1	2.5	7.3	3.5	25	6.5	2.3	9.0

Notations, F_σ etc. and A_σ etc., refer to Blue dye and Acid dye, respectively.

G_σ are given in Fig. 6. Good agreement between the calculated (Fig. 6) and the measured (Fig. 2) values shows that the behavior of dyes in mixture dyeing may be qualitatively explained by the knowledge of single dyeing, if it is possible to know the instability constant.

If the composition of complexes remains constant over the whole concentration range, K should be determined in principle even when the composition is not 1:1. In this way the amount of dyes adsorbed from mixture dyeing may be predicted. In the case of the mixture of Blue dye and Acid dye, however, the composition is gradually varied****, so the instability constant could not be obtained. Therefore, the amount of adsorption of the dyes from mixture dyeing can not be calculated by the above method. But it is expected that the difference between Fig. 1 and Fig. 2 may be understood qualitatively as follows: it is dependent directly on the extent of decrease in the effective dyebath concentration of Blue dye whether the reduction in adsorption of this dye is slow (Fig. 1) or rapid (Fig. 2) with an increase in the dyebath concentration of its partners. This fact may be attributed to the following two factors:

(a) The mole ratio of components in complexes.

(b) The instability constant of the complexes.

It is clear that the smaller the mole ratio (G_c/F_c or A_c/F_c), the greater the

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**** The spectroscopic measurements for the same mixture free from sodium chloride at room temperature show the same tendency: A_c/F_c gradually increases with an increase in the relative concentration of Acid dye.

TABLE III. EFFECT OF TEMPERATURE ON THE ADSORPTION OF BLUE DYE

G_σ/F_σ	T°C	$\Delta \ln F_\sigma'/\Delta T$	$-4\Delta \ln Na_\phi/\Delta T$	$\Delta(-\Delta\mu^\circ/\boldsymbol{R}T)/\Delta T$	$\Delta \ln F_\phi/\Delta T$
0.5	50 70	−0.0005	+0.0677	−0.100	−0.037
	70 90	+0.0154	+0.0708	−0.165	−0.079
5.0	50 70	+0.0137	+0.0118	−0.060	−0.034
	70 90	+0.1035	+0.0062	−0.120	−0.014
10.0	50 70	+0.0142	+0.0121	−0.045	−0.019
	70 90	+0.1097	+0.0129	−0.115	+0.008

decrease in effective dyebath concentration of Blue dye. If one considers only this point, it will apparently be expected from Tables I and II that the reduction of F_ϕ is slower in the case of the pair of Acid dye and Blue dye than that of Yellow dye and Blue dye. On the other hand, when the complexes have the same composition, the smaller K is, the greater should be the decrease in the effective dye bath concentration. For instance, it will be expected that in the case of the pair of Acid dye and Blue dye the value of K at a given temperature is greater than in the case of that of Yellow dye and Blue dye in a concentration range, in which only a 1 : 1 complex seems to be formed in both pairs[9]. Concerning the effect of temperature, the reduction in adsorption of a dye on addition of its partner will become smaller with temperature, since the value of K increases in general with the rise of temperature. This is clearly seen in Figs. 1 and 2.

The relation between the amount of Blue dye adsorbed from the mixture with Yellow dye and dyeing temperature, as shown in Fig. 3, is also remarkable. That is, the amount of Blue dye adsorbed from the mixture, which contains several times as much Yellow dye as Blue dye, tends to increase slightly with the rise of temperature. The interpretation of this result is rendered difficult, but it may be explained at least by the hypothesis of complex formation and the knowledge of single dyeing. In other words, if Na_σ and V are independent of temperature, the partial differentiation of Eq. 1 with respect to T leads to

$$\frac{\partial \ln F_\phi}{\partial T} = -4\frac{\partial \ln Na_\phi}{\partial T} + \frac{\partial \ln F_\sigma'}{\partial T} + \frac{\partial}{\partial T}\left(\frac{-\Delta\mu^0}{\boldsymbol{R}T}\right) \tag{4}$$

To see the correspondence of the equation with the results in Fig. 3, the value of each term at the right side of Eq. 4 was calculated for the interval of 20°C (50∼70 and 70∼90°C). If one takes 1×10^{-5} mol./l. as F_σ, 1 : 0.5, 1 : 5 and 1 : 10 as F_σ/G_σ, and 5×10^{-7}, 1×10^{-6} and 5×10^{-5} mol./l. as K of the 1 : 1 complex at 50, 70 and 90°C, respectively, then F_σ' at each temperature can be calculated from Eq. 3, and Na_ϕ and $-\Delta\mu^0$ can be obtained from Fig. 5, also. Therefore, the value of $\Delta \ln F_\phi/\Delta T$ can be obtained from Eq. 4. They are listed in Table III. The result agrees qualitatively with the relation between F_ϕ and the temperature shown in Fig. 3. It will be recognized here that the sign of $\partial \ln F_\phi/\partial T$ may be dependent chiefly on the relation between the second and the third terms. In other words, it may mostly be influenced by the dependence of the instability constant and the affinity on temperature.

Summary

1) The amount of dyes adsorbed by Cellophane from two mixture dyeings of Chlorazol Sky Blue FF and Chrysophenine G, and Chlorazol Sky Blue FF and p-nitroaniline → γ acid (α-coupling) was measured. Further, the amount in case of single dyeing was also measured.

2) It was assumed that the reduction in adsorption of dyes from mixture dyeing is due to an interaction between the two dyes in the dyebath, and that this interaction means only the formation of complexes. On this assumption, the instability constant in the case of the pair of Blue dye

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[9] A value of K of the mixture in aqueous solution of Blue dye and Acid dye calculated at room temperture for a concentration range, in which only a 1 : 1 complex seems to be formed, is 1.25×10^{-5} (Ref. 6) and that of the mixture of Blue dye and Yellow dye is 4×10^{-6} at 60°C (Ref. 3). If these values are compared with each other at the same temperature, the difference between them will become greater: K of the former may be much greater than that of the latter.

and Yellow dye was calculated, according to the mass action law, but it was impossible to calculate it in the case of the pair of Acid dye and Blue dye, because the composition of complexes of this pair was not constant.

3) How the amount of Blue dye adsorbed from mixture dyeing varies with the sort and the concentration of its partner dye and with the dyeing temperature was discussed from the standpoint of the instability constant and the affinity.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo