# The Adsorption of Dye Mixtures by Cellophane Sheet. II[1]. A Quantitative Discussion of the Adsorption of Dyes

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In the previous work[1], a method of quantitative discussion of the interaction between dyes in a binary mixture dyebath has been discussed on the assumption that the decrease in adsorption of dyes from mixture dyeing is due to interaction. Further, the behavior of dyes in mixture dyeing has been qualitatively explained from those of single dyeings, taking account of the interaction obtained by the above method.

In this paper, the single dyeings of Chlorazol Sky Blue FF and Chrysophenine G and their mixture dyeing have been carried out in detail, to discuss quantitatively their behavior in mixture dyeing. In the single dyeing, the surface layër volume in Vickerstaff's theoretical equation for adsorption[2] has been discussed to obtain constant values of the standard affinity. In the mixture dyeing, the observed amounts of adsorption of the dyes have been compared with those calculated on the basis of the information both about the single dyeing particularly discussed and about the interaction obtained from the single and the mixture dyeings by the method reported before[1].

### Experimental and Results

The single dyeings of Chlorazol Sky Blue FF (shortly called Blue dye) and Chrysophenine G (Yellow dye) and the mixture dyeing of them follow a method quite similar to that in the previous work[1].

In the single dyeings, the initial concentration ranged from $1\times10^{-6}$ to $1.5\times10^{-5}$ mol./l. for Blue dye and $1.25\times10^{-6}$ to $1\times10^{-4}$ mol./l. for Yellow dye, and in the mixture dyeing, that of Blue dye was fixed at about $1\times10^{-5}$ mol./l. and that of Yellow dye varied from $2.5\times10^{-6}$ to $1\times10^{-4}$ mol./l.

Each dyeing was carried out for three, two and one day* at 50°, 70° and 90°C, respectively. The concentration of sodium chloride (2 g./l.) was the same as that in the previous work.

Results for single dyeings are shown in Figs. 1 (Blue dye) and 2 (Yellow dye) in terms of the relation between logarithms of the final dyebath concentration (Blue dye, $F_\sigma$ mol./l.; Yellow dye, $G_\sigma$ mol./l.) and those of the amount of adsorption (Blue dye, $F_\phi$ mol./kg.; Yellow dye, $G_\phi$ mol./kg.) of the dyes. The affinities of Blue dye and Yellow dye ($-\Delta\mu^0_F$ cal./mol.; $-\Delta\mu^0_G$ cal./mol.) were calculated by Vickerstaff's equation with $V$=0.45 l./kg. These results are shown in Figs. 3 (Blue dye) and 4 (Yellow dye) in terms of the relation between

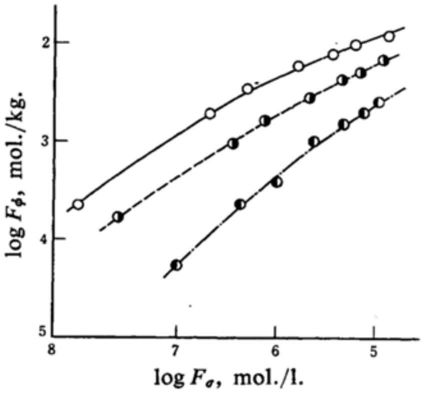


Fig. 1. Adsorption isotherms of Chlorazol Sky Blue FF on 'Cellophane' sheet at various temperatures: logarithmic plot of dyebath concentration and adsorption on the fiber.
—○— 50°C --◑-- 70°C ---◐--- 90°C

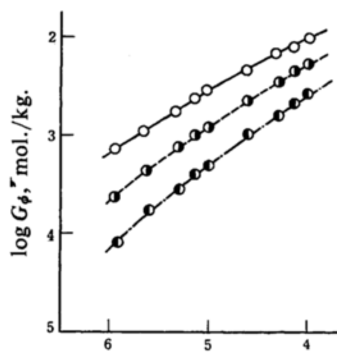


Fig. 2. Adsorption isotherms of Chrysophenine G on 'Cellophane' sheet at various temperatures: logarithmic plot of dyebath concentration and adsorption on the fiber.
—○— 50°C --◑-- 70°C ---◐--- 90°C

1) Part I of this series, Y. Horiki, Y. Tanizaki and N. Ando, This Bulletin, 33, 163 (1960).
2) R. H. Peters and T. Vickerstaff, *Proc. Roy. Soc. (London)* A192, 292 (1948).
* The dyeing time was ascertained to be sufficient to reach equilibrium at each temperature.

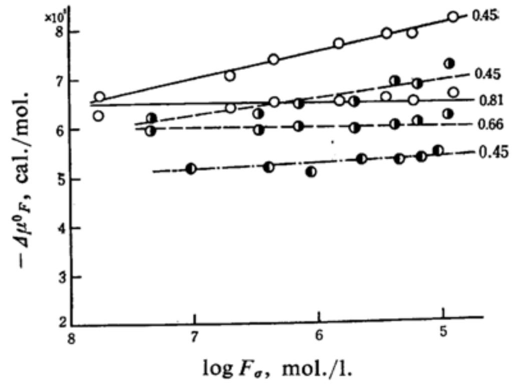


Fig. 3. Dependence of the standard affinity on dyebath concentration of Chlorazol Sky Blue FF at each temperature: plot of the standard affinity for logarithm of final dyebath concentration. The figures on each line indicate the surface layer volume (l./kg.) used in calculation.

—○— 50°C --◑-- 70°C --·◐·-- 90°C

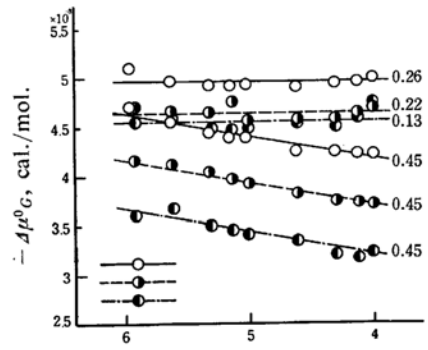


Fig. 4. Dependence of the standard affinity on dyebath concentration of Chrysophenine G at each temperature: plot of the standard affinity for logarithm of final dyebath concentration. The figure on each line indicates the surface layer volume (l./kg.) used in calculation.

the affinity and the logarithm of the final dyebath concentration. The relations of ($\log F_\phi \mathrm{Na}^4_\phi - \log F_\sigma \mathrm{Na}^4_\sigma$) and of ($\log G_\phi \mathrm{Na}^2_\phi - \log G_\sigma \mathrm{Na}^2_\sigma$) are shown in Figs. 5 and 6, respectively. It is recognized that they are nearly linear. Results of mixture dyeing, that is, the adsorptions of Blue dye ($F_\phi$ mol./kg.) and Yellow dye ($G_\phi$ mol./kg.), their effective dyebath concentrations obtained by the method reported before[1] ($F_\sigma'$ mol./l.; $G_\sigma'$ mol./l.), their dyebath concentrations which contributed to the interaction ($F_c$ mol./l.; $G_c$ mol./l.), and the ratios $G_\sigma/F_\sigma$ and $G_c/F_c$ are shown in Table I, together with the instability constant $K$ (mol./l.) calculated in the region where $G_\sigma/F_\sigma=0.8\sim1.1$, according to

$$K=\frac{F_\sigma'\cdot G_\sigma'}{\frac{F_c+G_c}{2}}=\frac{2F_\sigma'\cdot G_\sigma'}{F_c+G_c}=\frac{2(F_\sigma-F_c)(G_\sigma-G_c)}{F_c+G_c} \quad (1)$$

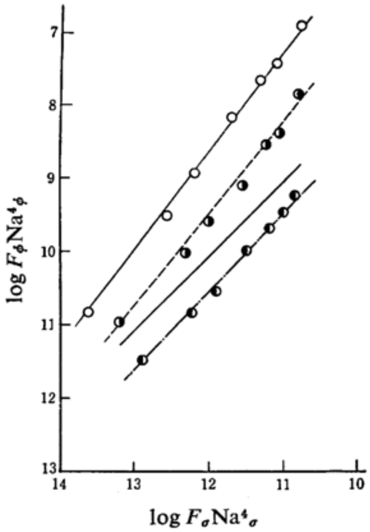


Fig. 5. Adsorption of Chlorazol Sky Blue FF on 'Cellophane' sheet at each temperature: plot of logarithm of ionic products in the fiber and in dyebath.

| | | $\alpha$ |
|---|---|---|
| —— | | 1.00 |
| —○— | 50°C | 1.32 |
| ---◑--- | 70°C | 1.20 |
| -·-◐-·- | 90°C | 1.05 |

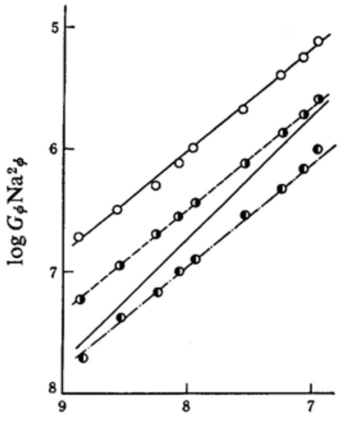


Fig. 6. Adsorption of Chrysophenine G on 'Cellophane' sheet at each temperature: Plot of logarithm of ionic products in the fiber and in dyebath.

| | | $\alpha$ |
|---|---|---|
| —— | | 1.00 |
| —○— | 50°C | 0.85 |
| ---◑--- | 70°C | 0.84 |
| -·-◐-·- | 90°C | 0.82 |

TABLE I

| $T$°C | Exp. No. | $F_\phi$ mol./kg. $\times 10^3$ | $F_\sigma$ mol./l. $\times 10^6$ | $F_\sigma{}'$ mol./l. $\times 10^6$ | $F_c$ mol./l. $\times 10^6$ | $G_\phi$ mol./kg. $\times 10^3$ | $G_\sigma$ mol./l. $\times 10^6$ | $G_\sigma{}'$ mol./l. $\times 10^6$ | $G_c$ mol./l. $\times 10^6$ | $G_\sigma/F_\sigma$ | $G_c/F_c$ | $K$ mol./l. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 10.36 | 9.46 | 7.5 | 2.0 | 0.03 | 2.53 | ? | ? | 0.27 | ? | |
| | 2 | 8.98 | 9.30 | 4.9 | 4.4 | 0.25 | 4.94 | ? | ? | 0.53 | ? | |
| | 3 | 7.76 | 9.64 | 3.2 | 6.4 | 0.45 | 6.91 | ? | ? | 0.72 | ? | |
| | 4 | 6.37 | 9.72 | 1.8 | 7.9 | 0.78 | 8.88 | 1.1 | 7.9 | 0.91 | 1.0 | $2.5\times10^{-7}$ |
| 50 | 5 | 4.87 | 9.78 | 0.91 | 8.9 | 1.00 | 10.92 | 1.8 | 9.1 | 1.12 | 1.0 | 1.8× 〃 |
| | 6 | 1.82 | 9.74 | 0.19 | 9.6 | 2.36 | 19.79 | 7 | 12.8 | 2.03 | 1.3 | |
| | 7 | 0.56 | 10.01 | 0.04 | 10.0 | 4.46 | 39.66 | 23 | 16.7 | 3.96 | 1.7 | |
| | 8 | 0.27 | 10.04 | 0.01 | 10.0 | 5.96 | 59.10 | 36 | 23.1 | 5.89 | 2.3 | |
| | 9 | 0.14 | 10.11 | 0.01 | 10.0 | 7.47 | 79.21 | 56 | 23.2 | 7.83 | 2.3 | |
| | 10 | 0.05 | 10.09 | ? | ≒10 | 9.33 | 98.90 | 83 | 15.9 | 9.80 | 1.6 | |
| | 1 | 5.33 | 9.82 | 6.8 | 3.0 | 0.07 | 2.53 | ? | ? | 0.26 | ? | |
| | 2 | 4.53 | 9.83 | 4.8 | 5.0 | 0.19 | 5.05 | 0.9 | 4.2 | 0.51 | 0.8 | $9.4\times10^{-7}$ |
| | 3 | 3.94 | 9.73 | 3.7 | 6.0 | 0.25 | 6.96 | 1.3 | 5.7 | 0.72 | 1.0 | 8.2× 〃 |
| | 4 | 3.40 | 9.78 | 2.9 | 6.9 | 0.40 | 8.90 | 2.2 | 6.7 | 0.91 | 1.0 | 9.4× 〃 |
| 70 | 5 | 2.87 | 9.91 | 2.0 | 7.9 | 0.51 | 10.91 | 2.9 | 8.0 | 1.10 | 1.0 | 7.3× 〃 |
| | 6 | 1.56 | 9.75 | 0.66 | 9.1 | 1.32 | 19.95 | 10 | 10.0 | 2.05 | 1.1 | 6.9× 〃 |
| | 7 | 0.72 | 9.92 | 0.25 | 9.7 | 2.34 | 39.61 | 25 | 14.6 | 3.99 | 1.5 | |
| | 8 | 0.44 | 9.92 | 0.14 | 9.8 | 3.18 | 59.77 | 43 | 16.8 | 6.02 | 1.7 | |
| | 9 | 0.29 | 10.01 | 0.09 | 9.9 | 3.92 | 79.75 | 61 | 18.8 | 7.97 | 1.9 | |
| | 10 | 0.20 | 9.97 | 0.06 | 9.9 | 5.47 | 99.33 | 100 | ? | 9.96 | ? | |
| | 1 | 1.96 | 9.64 | 6.8 | 2.8 | 0.09 | 2.51 | 1.3 | 1.2 | 0.26 | 0.4 | |
| | 2 | 1.87 | 9.74 | 6.2 | 3.5 | 0.10 | 4.98 | 1.5 | 3.5 | 0.51 | 1.0 | $2.7\times10^{-6}$ |
| | 3 | 1.72 | 9.77 | 5.4 | 4.4 | 0.18 | 7.48 | 2.8 | 4.7 | 0.77 | 1.1 | 3.3× 〃 |
| | 4 | 1.63 | 9.64 | 4.9 | 4.7 | 0.30 | 10.02 | 5.2 | 4.8 | 1.04 | 1.0 | 5.4× 〃 |
| 90 | 5 | 1.14 | 9.79 | 2.8 | 7.0 | 0.52 | 20.08 | 10.5 | 9.6 | 2.05 | 1.4 | |
| | 6 | 0.71 | 10.01 | 1.3 | 8.7 | 1.02 | 39.83 | 25 | 14.8 | 3.98 | 1.7 | |
| | 7 | 0.51 | 9.94 | 0.87 | 9.1 | 1.53 | 59.63 | 45 | 14.6 | 6.00 | 1.6 | |
| | 8 | 0.37 | 9.90 | 0.58 | 9.3 | 1.94 | 79.60 | 64 | 15.6 | 8.04 | 1.7 | |
| | 9 | 0.30 | 10.05 | 0.45 | 9.6 | 2.35 | 99.11 | 86 | 13.1 | 9.86 | 1.4 | |

## Discussion

The standard affinity of dye anions for the fiber in the single dyeing can be calculated theoretically by[2]

$$\log \frac{D_\phi \mathrm{Na}^z{}_\phi}{V^{z+1}} = \log D_\sigma \mathrm{Na}^z{}_\sigma + \left(\frac{-\Delta\mu^0}{RT}\right) \qquad (2)$$

$$\mathrm{Na}_\phi = D_\phi\left\{\frac{z}{2} + \left(\frac{z^2}{4} + \frac{V^2 \mathrm{Na}_\sigma \cdot \mathrm{Cl}_\sigma}{D^2{}_\phi}\right)^{1/2}\right\} \qquad (2')$$

where $D_\phi$ is the amount of adsorbed dye anions on the fiber at equilibrium (mol./kg.), $D_\sigma$, the dyebath concentration of dye anions at equilibrium (mol./l.), $\mathrm{Na}_\phi$, the concentration of the sodium ion in the fibre phase at equilibrium (mol./kg.), $\mathrm{Na}_\sigma$, $\mathrm{Cl}_\sigma$, the concentrations of the sodium and the chloride ions in the dyebath at equilibrium (mol./l.), $-\Delta\mu^0$, the standard affinity of dye anions for the fiber (cal./mol.), $z$, the valency of dye anions, $R$, $T$, the gas constant and the absolute temperature, and $V$, the surface layer volume of the fiber (l./kg.). However, the relation of Eq. 2 does not always come into being, depending on values employed as the surface layer volume, and it forms the following relations usually:

$$\log \frac{D_\phi \mathrm{Na}^z{}_\phi}{V^{z+1}} = \alpha \log D_\sigma \mathrm{Na}^z{}_\sigma + \left(\frac{-\Delta\mu^{0\prime}}{RT}\right) \qquad (3)$$

Hence, $-\Delta\mu^{0\prime}$ corresponding to the affinity in this equation does not show a constant value. This was also seen in the present results; the value of $\alpha$ obtained from the results of the single dyeing of Blue dye or Yellow dye by using $V=0.45$ l./kg. does not become unity, as is shown clearly by the relations of $\log F_\phi \mathrm{Na}_\phi{}^4 - \log F_\sigma \mathrm{Na}^4{}_\sigma$ and of $\log G_\phi \mathrm{Na}^2{}_\phi - \log G_\sigma \mathrm{Na}^2{}_\sigma$ in Figs. 5 and 6. Consequently, $-\Delta\mu^{0\prime}$ does not show constant values as shown in Figs. 3 and 4. Theoretically the affinity should remain constant. In order to discuss quantitatively the behavior of dyes in the mixture dyeing, it is desirable that $-\Delta\mu^{0\prime}$ obtained from the single dyeing should be constant. Now, let us assume simply that the reason why $\alpha$ is not unity is due to the improper value of $V$. If

$V'$ is put as the surface layer volume corresponding to $\alpha=1$, $V$ should be replaced by $V'$ in Eq. 2, and then $Na_\phi$ by $Na_\phi'$ (mol./kg.) corresponding to $V'$. Thus we obtain

$$\frac{1}{\alpha}\log\frac{D_\phi Na^z{}_\phi}{V^{z+1}}=\log\frac{D_\phi Na_\phi'^z}{V'^{z+1}} \tag{4}$$

Then, Eq. 3 becomes

$$\log\frac{D_\phi Na_\phi'^z}{V'^{z+1}}=\log D_\sigma Na_\sigma{}^z+\frac{1}{\alpha}\left(\frac{-\Delta\mu^0}{RT}\right) \tag{5}$$

Thus we shall obtain constant affinities by putting

$$\frac{1}{\alpha}\left(\frac{-\Delta\mu^{0\prime}}{RT}\right)=\frac{-\Delta\mu^0}{RT} \tag{6}$$

Such a surface layer volume $V'$ can be calculated as follows: from a graph of $\log D_\phi Na^z{}_\phi-\log D_\sigma Na^z{}_\sigma$ drawn by using any seemingly adequate value of $V$ (e. g. 0.45 l./kg.), we obtain a value of $\alpha$, and then putting it into Eq. 4 together with any two pairs of the results of single dyeing ($D_{\phi_1}$, $Na_{\phi_1}$) ($D_{\phi_2}$, $Na_{\phi_2}$), we have

$$\frac{1}{\alpha}\log\frac{D_{\phi_1}Na^z{}_{\phi_1}}{V^{z+1}}=\log\frac{D_{\phi_1}Na'^z{}_{\phi_1}}{V'^{z+1}} \tag{7}$$

$$\frac{1}{\alpha}\log\frac{D_{\phi_2}Na^z{}_{\phi_2}}{V^{z+1}}=\log\frac{D_{\phi_2}Na'^z{}_{\phi_2}}{V'^{z+1}} \tag{7'}$$

Thus the following equation is obtained,

$$\frac{Na'_{\phi_1}}{Na'_{\phi_2}}=\left(\frac{D_{\phi_1}}{D_{\phi_2}}\right)^{\left(\frac{1}{\alpha}-1\right)/z}\cdot\left(\frac{Na_{\phi_1}}{Na_{\phi_2}}\right)^{\frac{1}{\alpha}} \tag{8}$$

On the other hand, if each of ($D_{\phi_1}$, $Na'_{\phi_1}$) and ($D_{\phi_2}$, $Na'_{\phi_2}$) satisfies Eq. 2′, we obtain from Eqs. 8 and 2′

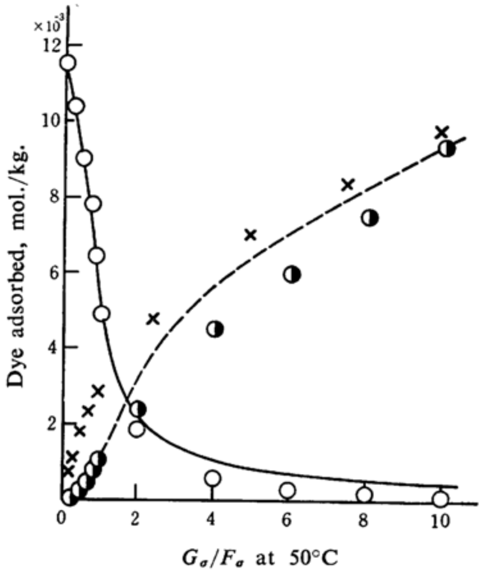

Fig. 7.

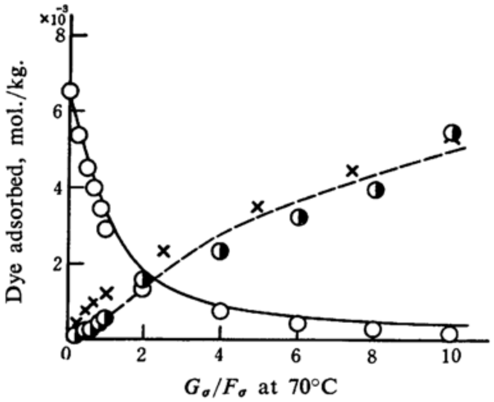

Fig. 8.

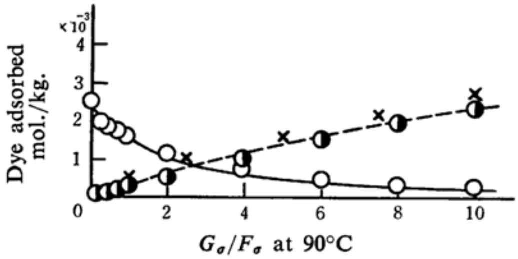

Fig. 9.

Figs. 7, 8 and 9. Adsorption isotherms of Chlorazol Sky Blue FF and Chrysophenine G in mixture dyeing at various temperatures: plot of adsorption on the fibre and ratio $G_\sigma/F_\sigma$; solid line, the curve of adsorption predicted theoretically of Chlorazol Sky Blue FF in mixture dyeing; broken line, the curve of adsorption predicted theoretically of Chrysophenine G in mixture dyeing.

○: The adsorption observed of Chlorazol Sky Blue FF in mixture dyeing.

◑: The adsorption observed of Chrysophenine G in mixture dyeing.

×: The adsorption observed of Chrysophenine G in single dyeing.

$$\frac{Na'_{\phi_1}}{Na'_{\phi_2}}=\frac{D_{\phi_1}\left\{\frac{z}{2}+\left(\frac{z^2}{4}+\frac{V'^2 Na_{\sigma_1}\cdot Cl_{\sigma_1}}{D^2{}_{\phi_1}}\right)^{1/2}\right\}}{D_{\phi_2}\left\{\frac{z}{2}+\left(\frac{z^2}{4}+\frac{V'^2 Na_{\sigma_2}\cdot Cl_{\sigma_2}}{D^2{}_{\phi_2}}\right)^{1/2}\right\}} \tag{9}$$

where $Na_{\sigma_1}$, $Cl_{\sigma_1}$, etc. denote the concentrations of the sodium and the chloride ion in the dyebath at equilibrium (mol./l.) respectively. When we solve Eq. 9 with respect to $V'$ and put it into Eq. 5, we may be able to obtain constant values of the standard affinity.

Now in practice, values of the surface layer volume $V'$ for the single dyeings of Blue dye and Yellow dye are obtained by use of $\alpha$ resulting from $V=0.45$ l./kg. and the affinities are calculated from Eqs. 5 and 6 by use of this $V'$. These results are shown in Table II, Figs. 3 and 4. " $-\Delta\mu^0_{\mathrm{mean}}$ " in the table denotes the mean values of adjusted affinities of Blue dye and Yellow dye. They give rather constant values**. Such adjustment of the surface layer volume so as to obtain a constant affinity means to treat $V$ as a parameter.

The observed amounts of adsorption of the dyes from the mixture dyeing are compared with those calculated by using the adjusted $-\Delta\mu^0_{\mathrm{mean}}$ (Table II) and the instability constant $K$ (Table I), which was obtained from the results of the single and the mixture dyeings as mentioned before[1], on the assumption

TABLE II

| Dye | $T$°C | $\alpha$ | $V'$ l./kg. | $-\Delta\mu^0_{\mathrm{mean}}$ cal./mol. |
|---|---|---|---|---|
| Blue dye | 50 | 1.32 | 0.81 | 6500 |
| | 70 | 1.20 | 0.66 | 6000 |
| | 90 | 1.05 | 0.45 | 5300 |
| Yellow dye | 50 | 0.85 | 0.26 | 4970 |
| | 70 | 0.84 | 0.22 | 4640 |
| | 90 | 0.82 | 0.13 | 4550 |

that the reduction in amounts of adsorption from mixture dyeing is mainly due to an interaction between both dyes in the dyebath. These results are shown in Figs 7, 8 and 9. However, on the supposition that only a one to one complex is formed over the whole concentration region of the dyes and that dye molecules which contribute to the complex formation have no relation to adsorption, the effective dyebath concentration of Blue dye $F'_{\sigma\mathrm{cal}}$ (hereafter " cal " is suffixed to calculated values) is obtained from Eq. 10

$$F'_{\sigma\mathrm{cal}}=1/2\{(G_\sigma-a)^2+(b^2-a^2)\}^{1/2}+1/2(a-G_\sigma) \tag{10}$$

where $a=F_\sigma-K$ and $b=F_\sigma+K$, and the mean value of the instability constant shown in Table I is used as $K$, i. e. $2\times10^{-7}$, $8\times10^{-7}$ and $4\times10^{-6}$ (mol./l.) at 50°, 70° and 90°C, respectively. The final dyebath concentration of Blue dye and Yellow dye in Table I are used as $F_\sigma$ and $G_\sigma$ in Eq. 10.

The effective dyebath concentration of Yellow dye $G'_{\sigma\mathrm{cal}}$ is obtained from

$$G'_{\sigma\mathrm{cal}}=G_\sigma-G_{c\mathrm{cal}}=G_\sigma-(F_\sigma-F'_{\sigma\mathrm{cal}})=G_\sigma-F_{c\mathrm{cal}} \tag{11}$$

The amount of adsorption of both dyes are calculated by the following equations, on the assumption that the affinity of each dye does not change in the mixture dyeing.

$$F_{\phi\mathrm{cal}}=F'_{\sigma\mathrm{cal}}\mathrm{Na}^{-4}{}_{F\phi\mathrm{cal}}\mathrm{Na}^4{}_\sigma V_F'^5\times\exp\left(\frac{-\Delta\mu^0{}_{F\mathrm{mean}}}{RT}\right) \tag{12}$$

$$G_{\phi\mathrm{cal}}=G'_{\sigma\mathrm{cal}}\mathrm{Na}^{-2}{}_{G\phi\mathrm{cal}}\mathrm{Na}^2{}_\sigma V_G'^3\times\exp\left(\frac{-\Delta\mu^0{}_{G\mathrm{mean}}}{RT}\right) \tag{12'}$$

where the values for $\mathrm{Na}_{F\phi\mathrm{cal}}$ and $\mathrm{Na}_{G\phi\mathrm{cal}}$ are approximately obtained from the equations derived by eliminating $D_\phi$ in Eqs. 2 and 2',

$$\mathrm{Na}^3{}_{F\phi\mathrm{cal}}(\mathrm{Na}^2{}_{F\phi\mathrm{cal}}-V_F'^2\mathrm{Na}_\sigma\cdot\mathrm{Cl}_\sigma)=4\mathrm{Na}_\sigma{}^{-4}F'_{\sigma\mathrm{cal}}V_F'^5\exp\left(\frac{-\Delta\mu^0{}_{F\mathrm{mean}}}{RT}\right) \tag{13}$$

$$\mathrm{Na}_{G\phi\mathrm{cal}}(\mathrm{Na}^2{}_{G\phi\mathrm{cal}}-V_G'^2\mathrm{Na}_\sigma\cdot\mathrm{Cl}_\sigma)=2\mathrm{Na}_\sigma{}^{-2}G'_{\sigma\mathrm{cal}}V_G'^3\exp\left(\frac{-\Delta\mu^0{}_{G\mathrm{mean}}}{RT}\right) \tag{13'}$$

where the values of $V_F'$, $V_G'$, $-\Delta\mu^0{}_{F\mathrm{mean}}$ and $-\Delta\mu^0{}_{G\mathrm{mean}}$ are obtained from the respective values at the various temperatures shown in Table II.

It is brought out from these results that the observed amounts of adsorption of the dyes agree well with those calculated over the whole range of concentration at 90°C (Fig. 9); this means that the behavior of the dyes in mixture may be explained quantitatively by the formation of a 1 : 1 complex in the dyebath. Though both values calculated and observed show considerably good agreement at 70 and 50°C, too, some deviation is recognized at these temperatures in the range where $2\lesssim G_\sigma/F_\sigma\lesssim8$. It may be due to the fact that where $G_\sigma/F_\sigma\geqq2$, the dyes form not only one to one complex, but higher complexes richer in Yellow dye (may be one to two), which promote the reduction of adsorption***. In the region $G_\sigma/F_\sigma\approx10$, the observed adsorption of Yellow dye tends to approach that in the single dyeing. This will be explained by the thought that even if the composition of complexes becomes completely one to two, Yellow dye may behave as in the single dyeing, because of its comparatively higher concentration than

** Standing has discussed the value of $V$ for Chrysophenine G ($z=2$) using the so-called $p$-$q$ equation (*J. Text. Inst.*, **45**, T 21 (1954)). With his method, however, the calculation for Chlorazol Sky Blue FF ($z=4$) becomes complicated. Hence in this work, $V$ was adjusted as above. The results for Chrysophenine G are considerably approximated to his result.

*** It has been recognized by spectral measurements that a 1 : 2 complex richer in Yellow dye is also formed in the mixture of Blue and Yellow dye at room temperature (T. Kobayashi, Y. Tanizaki and N. Ando., This Bulletin, **33**, 661 (1960)). On the other hand, it has been concluded that only a one to one complex is formed at 60°C (A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Col.*, **72**, 268 (1956)).

However, the spectral measurements for the mixture solution in the presence of sodium chloride at high temperature has not yet been carried out, so the composition of complexes may be open to discussion.

that of Blue dye. On the other hand, since $F_a$ is almost constant, the formation of complexes and their compositions may have considerable influence on the adsorption of Blue dye with an increase of Yellow dye. In fact, the observed values of adsorption of Blue dye shown in Figs. 7 and 8 are small compared with those calculated on the basis of the formation of only a one to one complex.

Thus the behavior of dyes in the mixture dyeing may be well explained quantitatively by the method mentioned above if both dyes interact with each other (complex formation) in the dyebath. If further information on these matters, i. e. on the single dyeing and the interaction, is obtained hereafter, this problem will be treated more clearly.

**Summary**

1. The single dyeings of Chlorazol Sky Blue FF and Chrysophenine G and the mixture dyeing of them were carried out at 50, 70 and 90°C.

2. In the single dyeing, the surface layer volume in Vickerstaff's equation was adjusted so as to obtain constant values of the standard affinity.

3. In the mixture dyeing, the behavior of dyes was explained quantitatively on the basis of the information of the single dyeing and the interaction between both dyes in the dyebath.

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