Absorption Spectra of Dyes. III[1]. *On the Composition of Complexes Formed in Mixtures of Chlorazol Sky Blue FF and p-Nitroaniline → γ Acid in Aqueous Solution*[*]

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The fact that complexes are formed between some kinds of dyes in aqueous solution has been revealed by means of spectroscopic measurements[2-4], and the mixtures of some direct dyes have been measured qualitatively in order to investigate the composition of the complexes formed[3,4].

The authors reported in the previous paper[1] that the mixtures of Chlorazol Sky Blue FF and some acid dyes, *p*-X-aniline → γ acid (X=H, CH_3, OCH_3, Cl or NO_2), did not show additive spectra in aqueous solution at room temperature, and that, of these mixtures, a pair of Chlorazol Sky Blue FF and *p*-nitroaniline → γ acid underwent the greatest change in spectrum. In the present paper the authors selected the combination of Chlorazol Sky Blue FF with *p*-nitroaniline → γ acid and investigated its spectrum at 620 mμ where the most remarkable change was seen in the whole region measured, in order to obtain some information about the composition of the complexes formed.

Experimental

Materials.—All the dyes used are the same as those used in the previous paper[1].

Preparation of Samples.—The dye solutions were prepared by using conductivity water whose specific conductivity was about 3.5×10^{-7} mho. All of the concentrations were determined by weight.

Absorption Spectra. — All the absorption spectra of the dyes in aqueous solution were measured by means of the Shimadzu QB-50 or QR-50 spectrophotometer at room temperature. Absorption cells were about 0.2 to 5 cm. thick.

Results

Hereafter Sky Blue will stand for Chlorazol Sky Blue FF, and NO_2-α for the acid dye made by coupling diazotized *p*-nitroaniline with γ acid in acid, and NO_2-β for the same in alkali.

It has already been shown[1] that the absorption spectrum of the mixture of Sky Blue and NO_2-α or NO_2-β in aqueous solution does not coincide with the sum of the spectra of individual dye, and this non-additivity is the most remarkable in the neighborhood of 620 mμ in wavelength. This spectral change is characterized by a marked decrease in optical density, with a slight shift of absorption maxima to longer wavelengths. For example, the absorption spectra of solutions containing

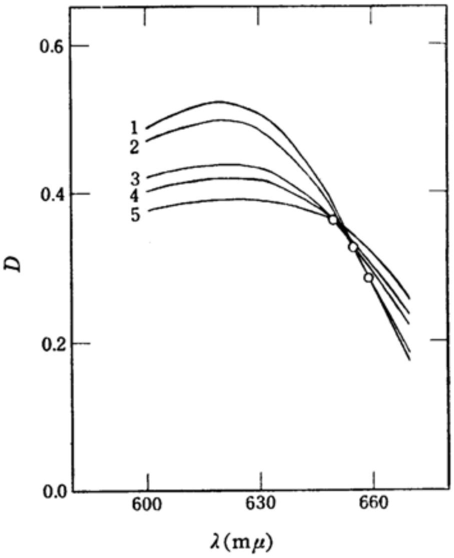

Fig. 1. Absorption spectra of mixtures of Sky Blue and NO_2-α in aqueous solution at room temperature. The concentration of Sky Blue is 1.41×10^{-5} mol./l., and that of NO_2-α is $1=2.72\times10^{-6}$, $2=6.98\times10^{-6}$, $3=2.11\times10^{-5}$, $4=3.51\times10^{-5}$ and $5=8.36\times10^{-5}$ mol./l. The absorption of NO_2-α alone is subtracted from each curve.

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[1] Part II of this series, Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 119 (1959).

[*] This was represented before the 11th Annual Meeting of the Chemical Society of Japan, April 1958.

[2] S. M. Neale and W. A. Stringfellow, *J. Soc. Dyers Col.*, **59**, 241 (1943).

[3] D. R. Lemin and T. Vickerstaff, *Trans. Faraday Soc.*, **43**, 491 (1947).

[4] A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Col.*, **72**, 268 (1956).

a given amount of Sky Blue and different amounts of NO_2-α are illustrated in Fig. 1, in which each absorption of NO_2-α alone is subtracted from that of the corresponding mixture. The figure shows that the spectra obviously indicate no isobestic point and the intersections of the adjacent curves are gradually shifted to shorter wavelengths. Therefore, it is clear that the formation of only a 1:1 complex does not adequately explain the data over the whole concentration range measured. Plotting the observed optical density, D, of this mixture at 620 mμ in relation to the concentration of NO_2-α, we obtain the curves as shown in Fig. 2, where the concentrations of Sky Blue indicated by the curves I and II are 6.02×10^{-6} and 1.41×10^{-5} mol./l., respectively. Inspection of these curves shows that in either case the optical density decreases with the concentration of NO_2-α to the amount about four times as great as that of Sky Blue, and then increases with the further increase of NO_2-α. The same

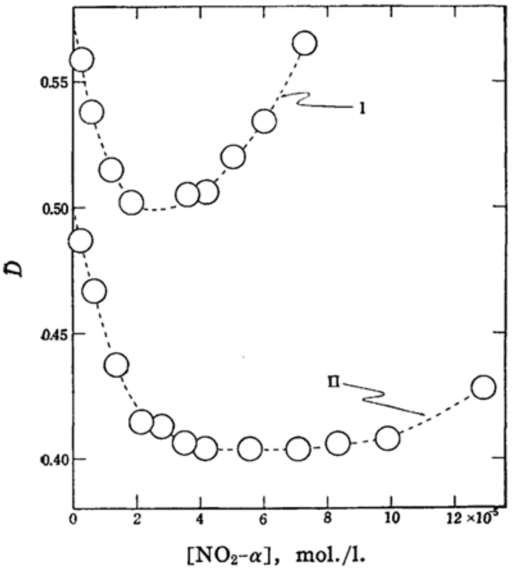

Fig. 2. The relation between the observed optical density of the combination of Sky Blue with NO_2-α and the concentration of NO_2-α at 620 mμ.

	The concentration of Sky Blue (mol./l.)	Cell (cm.)
I	6.02×10^{-6}	1
II	1.41×10^{-5}	0.399

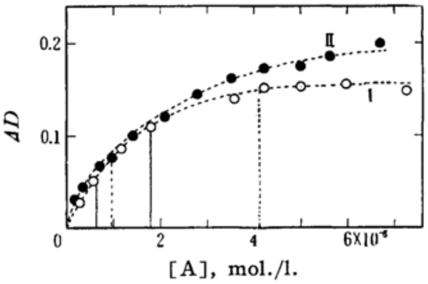

Fig. 3. The relation between the difference in density, ΔD, and the concentrations of the acid dyes at 14∼16°C. 1 cm. cell, $\lambda=620$ mμ. I: The mixture of NO_2-α and Sky Blue of 6.02×10^{-6} mol./l. II: The mixture of NO_2-β and Sky Blue of $7.15\times^{-6}$ mol./l.

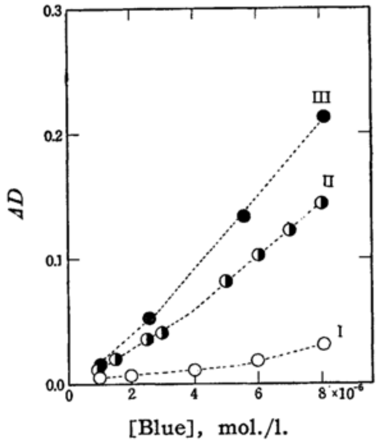

Fig. 4. The relation between the difference in density, ΔD, of the combination of Sky Blue with NO_2-α and the concentration of Sky Blue at 14∼16°C. 1 cm. thick, $\lambda=620$ mμ. The concentration of NO_2-α is $I=2.00\times10^{-6}$, $II=2.02\times10^{-5}$ and $III=6.41\times10^{-5}$ mol./l.

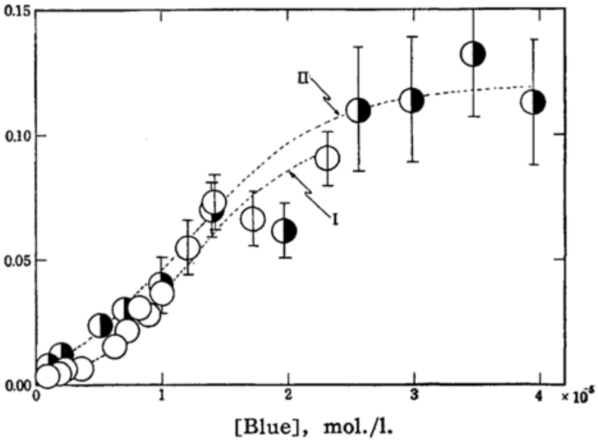

Fig. 5. The relation between the difference in density, ΔD, of the combination of Sky Blue with NO_2-α and the concentration of Sky Blue at 20∼22°C. 1 cm. thick, $\lambda=620$ mμ. The concentration of NO_2-α is $I=4.0\times10^{-6}$ and $II=5.97\times10^{-6}$ mol./l.

tendency was also observed in the mixture of Sky Blue and $NO_2-\beta$.

Now, let us consider the difference between the sum of densities of its components and that of the mixture, ΔD. The relation between ΔD and the concentration of $NO_2-\alpha$ or of $NO_2-\beta$ for a given concentration of Sky Blue is shown in Fig. 3. Both the curves in the figure curve upwards in the whole region and are inclined to approach certain values.

On the other hand, corresponding series of measurements were also carried out with mixtures containing various amounts of Sky Blue and given amounts of $NO_2-\alpha$, and the results are shown in Figs. 4 and 5. Here celles were selected so as to make values of density fall in 0.3 to 0.7, but all the observed values were converted into those for 1 cm. cell. Similarly, Fig. 4 indicates the relation between ΔD at 620 mμ and the concentration of Sky Blue, where the curves I, II and III correspond to the concentration of $NO_2-\alpha$ 2.00×10^{-6}, 2.02×10^{-5} and 6.41×10^{-4} mol./l., respectively. Fig. 5 shows the same relation as that in Fig. 4, but the curves I and II correspond to the concentrations of $NO_2-\alpha$, 4.0×10^{-6} and 5.97×10^{-6} mol./l. The optical densities were measured at about 21°C unlike the former case (at about 15°C). It will be seen at once from these curves that the higher the concentration of acid dye, the more remarkable the difference (Figs. 4 and 5), and that each curve bends downwards and upwards relatively to the low and high concentrations of Sky Blue, respectively (Fig. 5). Moreover, its point of inflexion moves towards a smaller value of concentration of Sky Blue in accordance with an increase in that of $NO_2-\alpha$. These are distinctly different from the case of the curves of ΔD-concentration of $NO_2-\alpha$ or ΔD-concentration of $NO_2-\beta$.

Discussion

Lemin and Vickerstaff[3] showed by the spectroscopic measurement that Chlorazol Sky Blue FF and Durazol Red 2B formes a 1:1 complex in aqueous solution at room temperature. On the other hand, Derbyshire and Peters[4] examined the mixture of Chlorazol Sky Blue FF and Chrysophenine G in aqueous solution by the spectroscopic and calorimetric measurements and concluded that the formation of a 1:1 complex occurs to an appreciable extent even at 90°C, while higher complexes are formed to a certain extent in the presence of an excess of Chrysophenine G. Now, as for the present case, it was stated in the last section that the formation of a 1:1 complex does not explain all the spectral change, judging from the fact that the absorption spectra of solutions containing Sky Blue and $NO_2-\alpha$ showed no isosbestic point anywhere over the region measured (Fig. 1).

The fact that most direct dyes aggregate more or less in aqueous solution and that this aggregation is increased by adding neutral salts has been confirmed by measuring conductivity, absorption spectra, etc.[5] And it has also been recognized that the absorption spectrum of Sky Blue in aqueous solution does not obey Beer's law[3]. In addition, it can safely be considered as a matter of course that another dye added to Sky Blue solution exerts such a salt effect on this dye. In spite of these facts, however, it will be assumed here that the effect of the self-aggregation of the individual dye, which is induced by its increased concentration or by the addition of another dye, can be disregarded as compared with the effect of the complex formation, because the change in optical density of either component caused by increasing its concentration was of comparatively small magnitude compared with that produced by mixing[**]. Further the change in density of Sky Blue produced by the salt effect of the acid dyes can also be disregarded on account of the fact that an addition of sodium

TABLE I. VARIATION OF MOLAR EXTINCTION COEFFICIENT OF CHLORAZOL SKY BLUE FF IN AQUEOUS SOLUTION AT ROOM TEMPERATURE

1 cm. thick, $\lambda=620$ mμ

Solution (mol./l.)	Molar extinction coefficient
5.10×10^{-6}	$9.3_9\times10^4$
9.97×10^{-6}	9.5_2 〃
1.99×10^{-5}	9.3_0 〃
2.99×10^{-5}	9.3_0 〃
3.97×10^{-5}	9.1_1 〃

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[5] C. Robinson and J. L. Moilliet, *Proc. Roy. Soc.* (*London*), **A143**, 630 (1934); E. Valkó, *Trans. Faraday Soc.*, **31**, 230 (1935); C. Robinson, *Proc. Roy. Soc.* (*London*), **A148**, 681 (1935); N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **64**, 1192, 1431 (1943); Y. Tanizaki and N. Ando, ibid., **78**, 343 (1957).

[**] The variation of the molar extinction coefficient of Sky Blue with respect to its concentration is shown in Table I. The measurement was carried out at 620 mμ over a range of concentration up to 3.97×10^{-5} mol./l. This table shows that the deviation from Beer's law is negligible. On the other hand, the aggregation of the acid dye itself, even if it occurs, could be disregarded, because its absorption at 620 mμ is very small.

TABLE II. OPTICAL DENSITY OF CHLORAZOL SKY BLUE FF (6.66×10^{-6} mol./l.) IN SODIUM CHLORIDE SOLUTION AT ROOM TEMPERATURE

1 cm. thick, $\lambda=620$ mμ

Sodium chloride (mol./l.)	Optical density
0	0.62_3
5.23×10^{-6}	0.61_6
1.00×10^{-5}	0.62_1
5.02×10^{-5}	0.61_6
1.02×10^{-4}	0.62_3

chloride to Sky Blue solution, in a range of concentrations comparable to those of the acid dyes used here, showed no significant change in optical density of Sky Blue***. Based on these assumptions, the observed result will be discussed as follows.

Now, in order to investigate the composition of the complexes formed, let us suppose m mol. of Sky Blue, B, and n mol. of any acid dye, A, have produced one mole of complex, C, in solution, that is,

$$m\mathrm{B} + n\mathrm{A} \rightleftarrows \mathrm{C}$$

According to the law of mass action, we can rewrite this as follows:

$$K=[\mathrm{C}]/([\mathrm{B}]-m[\mathrm{C}])^m([\mathrm{A}]-n[\mathrm{C}])^n \quad (1)$$

where [C], [B] and [A] mean the concentration in mol./l. of the complex and the initial concentrations of Sky Blue and the acid dye, respectively; and K is the equilibrium constant. When the absorption layer is regarded as unity, the observed optical density, D_{obs}, at any wavelength of a mixture will be

$$D_{\mathrm{obs}}=([\mathrm{B}]-m[\mathrm{C}])\varepsilon_{\mathrm{B}} + ([\mathrm{A}]-n[\mathrm{C}])\varepsilon_{\mathrm{A}}+[\mathrm{C}]\varepsilon_{\mathrm{C}}$$

where ε_{B}, ε_{A} and ε_{C} signify the molar extinction coefficients of Sky Blue, the acid dye and the complex, respectively. On the other hand, the sum of optical densities of the components, D_{sum}, is

$$D_{\mathrm{sum}}=[\mathrm{B}]\varepsilon_{\mathrm{B}}+[\mathrm{A}]\varepsilon_{\mathrm{A}}$$

so the difference, ΔD, becomes

$$\Delta D=(m\varepsilon_{\mathrm{B}}+n\varepsilon_{\mathrm{A}}-\varepsilon_{\mathrm{C}})[\mathrm{C}] \quad (2)$$

Since the molar extinction coefficients may be assumed to be unvarying, $(m\varepsilon_{\mathrm{B}}+n\varepsilon_{\mathrm{A}}-\varepsilon_{\mathrm{C}})$ can be described as a constant, k, provided that m and n are not changed in the entire concentration range of the dyes. As [C] is a function of [B] and [A] (Eq. 1), ΔD can be expressed as a function of them. According to the usual method[3)], K and k can be determined. A calculated value of K by making use of the observed values of optical density indicated by full lines in Fig. 3 was 8.0×10^4 for the mixture of Sky Blue and $\mathrm{NO_2}$-α when $m=n=1$. K values calculated by various observed optical densities were not so different from one another. Now, in order to investigate the relation between ΔD and the concentration of $\mathrm{NO_2}$-α, curves were drawn in accordance with Eq. 2. The results are shown in Fig. 6, in which the full lines indicate the calculated ones and the circles the corresponding observed values. From the figure it will be seen at once that the curves of $m=n=1$, namely of a 1 : 1 complex, suit the observed values comparatively well. A minute observation shows, however, that the calculated values are somewhat greater than the observed ones where the concentration of $\mathrm{NO_2}$-α is higher than that of Sky Blue. As Derbyshire and Peters reported[4)], while Chlorazol Sky Blue FF and Chrysophenine G form a 1 : 1 complex in aqueous solution, they form higher complexes richer in Chrysophenine G in presence of an excess of this dye. If this happens in the present case and higher complexes richer in the acid dye are formed, a curve of $m=1$ and $n=2$,

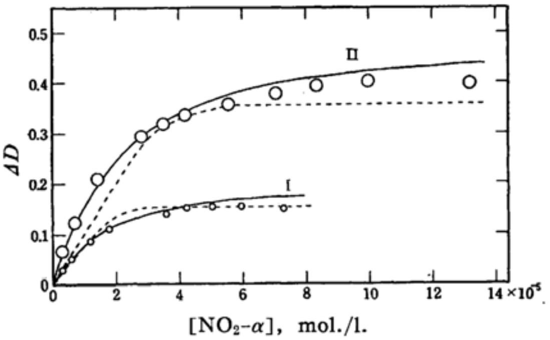

Fig. 6. The comparison between the differences observed and calculated by Eq. 2 for the mixtures of Sky Blue and $\mathrm{NO_2}$-α at 15°C. 1 cm. thick, $\lambda=620$ mμ. The concentration of Sky Blue is I$=6.02\times10^{-6}$ and II$=1.41\times10^{-5}$ mol./l. The full lines signify calculated 1 : 1 curves ($K=8.0\times10^4$), the dotted lines 1 : 2 curves ($K=7.1\times10^{10}$) and the circles the corresponding observed values.

*** As is shown in Table II, the effect of sodium chloride on Sky Blue solution in a range of concentrations comparable to those of the acid dyes used here is not so great as can be observed, so we leave the salt effect by the acid dye out of consideration.

namely of a 1:2 complex, should fit the observed values better than the 1:1 curve in the higher concentration region of the acid dye. The 1:2 curves ($K=7.1\times10^{10}$ which was calculated by making use of the observed values of optical density shown by the dotted lines in Fig. 3) are indicated by the dotted lines in Fig. 6. These curves differ extremely from the observed ones in the region where the 1:1 curve was rather suitable, but they are more suitable in the higher concentration range of the acid dye where the 1:1 complex curve has not fitted well. These facts suggest that a 1:1 complex is formed first and then higher complexes richer in the acid dye are formed with an increase of its concentration. If this is the case, the region of low concentration of the acid dye in the mixtures containing a given amount of Sky Blue should correspond to that of high concentration of Sky Blue in the mixtures containing a given amount of the acid dye. Actually, the curves of ΔD-concentration of Sky Blue (Figs. 4 and 5) are obviously different in shape from the curves of ΔD-concentration of NO_2-α, and become similar to the 1:1 curve in a region of high concentration of Sky Blue. Probably all the experimental results would be explained by a combination of a 1:1, a 1:2 and other complexes, or by a combination of several complexes different in their compositions. Exactly the same result has been obtained in the mixture of Sky Blue and NO_2-β. It is concluded here that one kind of complex does not explain all the exprimental data, and the comparison between the calculated and observed curves shows that a 1:1 complex occurs to a greater extent over a range of relatively low concentration of acid dye and that higher complexes richer in the acid dye may be formed in the presence of an excess of it.

Summary

1. The change in spectrum at 620 mμ of the mixture of Chlorazol Sky Blue FF and p-nitroaniline→γ acid in aqueous solution was measured in detail at room temperature, by varying the concentration of the component dyes.

2. On the assumption that the spectral change is due to the complex formation, the composition of complexes was discussed by comparing the observed and the calculated difference in optical density.

3. It may be supposed that a 1:1 complex occurs to a great extent over a range of low concentration of p-nitroaniline→γ acid as compared with that of Chlorazol Sky Blue FF, and that higher complexes are formed in the presence of an excess of the acid dye.

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