Absorption Spectra of Dyes. IV[1]. *Absorption Spectra of Mixtures of Chlorazol Sky Blue FF and Dyes Prepared from Sulfanilic Acid and Cresidine*

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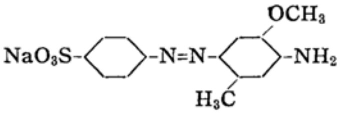
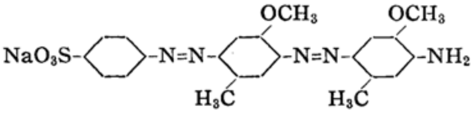
(Received December 19, 1958)

In the previous papers the authors have reported that binary mixtures of Chlorazol Sky Blue FF and certain monoazo acid dyes in aqueous solution show non-additivity in absorption spectrum at room temperature, explained qualitatively the spectral change assuming the formation of loose complexes[2], and then discussed their compositions[1]. In the present paper, absorption spectra of the binary mixtures in aqueuos solution of Chlorazol Sky Blue FF, as the one component, and dyes prepared from sulfanilic and cresidine, as the other, were analyzed, and the result obtained was examined.

Experimental

Dyes.—Chlorazol Sky Blue FF (called Sky Blue) is the same as used before[1,2]. SC_1 and SC_2 will signify the dye obtained by coupling diazotized sulfanilic acid with cresidine and that obtained by coupling diazotized SC_1 with cresidine. Their structures are as follows:

SC_1 

SC_2 

Both of them are carefully prepared from purified intermediates. SC_1 was purified by the recrystallization from water and SC_2 by the Robinson and Mills' method until no change in spectrum was observed. It was noticed that the solubility of SC_2 in water is extremely dependent on pH, and that its flocculent precipitate was easily produced by carbon dioxide from the air. The dye solutions, therefore, were once heated in order to remove carbon dioxide.

Measurements of Absorption Spectra.—All the absorption spectra of the dyes in aqueous solution were measured by means of the Shimadzu QR-50 spectrophotometer at room temperature. Absorption cells used were 0.2, 0.5 and 1 cm. thick. All the experimental values were converted into those corresponding to 1 cm. cell.

Results

The absorption spectrum of a mixture of Sky Blue (7.44×10^{-6} mol./l.) and SC_1 (3.58×10^{-5} mol./l.) is shown by a full line in Fig. 1, together with each spectrum of Sky Blue (curve I) and of SC_1 (curve II). The sum (curve III) of curves I and II coincides completely with the observed one (curve IV) in the whole region measured. The additivity in spectrum, however, does not come into being in the mixtures containing a great excess of SC_1. The results are given in Fig. 2, where the dotted line shows the absorption spectrum of Sky Blue alone (7.42×10^{-6} mol./l.) and curves I and II those of mixtures containing Sky Blue and SC_1 49.4 and 137 times as much as Sky Blue, respectively. In this wavelength region, SC_1 does not absorb light. As this change in spectrum is similar to that of certain benzidine disazo dyes like Sky Blue caused by the salt effect[3], it is supposed that it may be due to the self-aggregation of Sky Blue. Then the variation in optical density at 620 mμ of Sky Blue (7.42×10^{-6} mol./l.) in sodium chloride solution was examined, in order to investigate whether or not the change

TABLE I. VARIATION OF OPTICAL DENSITY OF CHLORAZOL SKY BLUE FF (7.42×10^{-6} mol./l.) IN SODIUM CHLORIDE SOLUTION AT 27°C. 1 cm. cell, $\lambda=620$ mμ

Sodium chloride (mol./l.)	Ratio of sodium chloride to Sky Blue	Optical density
0	0	0.73_4
4.05×10^{-4}	54.6	0.73_1
1.01×10^{-3}	136	0.73_0
1.05×10^{-2}	1415	0.70_9

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[1] Part III of this series, T Kobayashi, Y Tanizaki and N. Ando, This Bulletin, **32**, 675 (1959).

[2] Y. Tanizaki, T. Kobayashi and N. Ando, ibid., **32**, 119 (1959).

[3] Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 343 (1957).

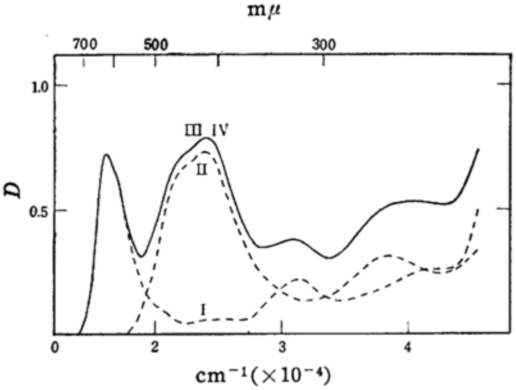

Fig. 1. Absorption spectra of Sky Blue, SC_1 and their mixture in aqueous solution at room temperature (27°C). 1 cm. cell.
I: Sky Blue (7.44×10^{-6} mol./l.)
II: SC_1 (3.58×10^{-5} mol./l.)
III: Sum of curves I and II
IV: Mixture

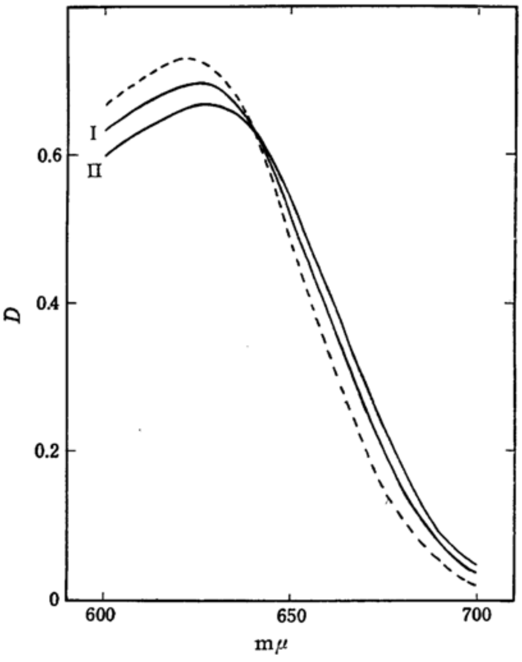

Fig. 2. Absorption spectra of mixtures of Sky Blue (7.42×10^{-6} mol./l.) and SC_1 in aqueous solution at room temperature (27°C). 1 cm. cell.
Dotted line: Sky Blue alone
I: The ratio of concentrations of Sky Blue and SC_1 is 49.4
II: The ratio is 137

is due to the salt effect of SC_1. The results are shown in Table I. It shows clearly that no significant departure from Beer's law is observed, even though the amount of sodium chloride becomes 140 times as much as that of Sky Blue. Therefore, we must consider that the spectral change shown in Fig. 2 is not due to the self-aggregation of Sky Blue caused by the salt effect of SC_1 added, but due to the interaction between the two dyes. It will be seen that the spectra pass through an isosbestic point at about 640 mμ, where the absorption of SC_1 does not appear (Fig. 1). This suggests that one Sky Blue molecule interacts with SC_1 molecules, or that $1:n$ complexes are formed. But the number n of SC_1 component in one complex molecule has not been known. These results mean that even if the additive spectrum appears in an equimolar or nearly equimolar mixture, the spectrum of the same mixture will often become non-additive with an increase of one component, and the interaction between the two components will occur.

The absorption spectrum of a mixture of Sky Blue and SC_2 is given in Fig. 3, where curves I and II show each absorption spectrum of Sky Blue and of SC_2, curve III the sum of them, and curve IV the observed one of the mixture. Inspection of them shows that the observed curve is weaker in intensity than the resultant curve both in the neighborhood of 620 mμ (the first band of Sky Blue) and at absorptions in the ultraviolet region, but stronger in the neighborhood of the first band of SC_2 (505 mμ).

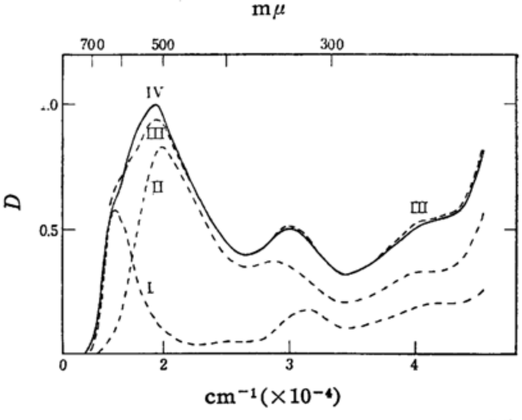

Fig. 3. Absorption spectra of Sky Blue, SC_2 and their mixture in aqueous solution at room temperature (30°C). 1 cm. cell.
I: Sky Blue (5.90×10^{-6} mol./l.)
II: SC_2 (3.01×10^{-5} mol./l.)
III: Sum of curves I and II
IV: Mixture

This spectral change was more systematically examined by varying the concentration of SC_2 and keeping that of Sky

Blue constant (5.90×10^{-6} mol./l.). The results are shown in Fig. 4, in which each absorption of SC_2 is subtracted from the corresponding observed curve. The curves in the figure pass through a well-defined isosbestic point at about 650 mμ; this means that one Sky Blue molecule interacts with a molecule or molecules of SC_2.

On the other hand, the relation between the concentration of SC_2 added and the difference between the sum of optical densities of the components and that of the mixture, ΔD, at 620 mμ is plotted by white circles in Fig. 5. Now, if a 1:1 complex is assumed to be formed in the solution, and if the mass action law is applied to it, an equilibrium constant, K, will be obtained by the method mentioned before[1]. Thus the obtained value of K was 3.8×10^4 at 30.5°C. Here were used the observed values of ΔD, when the concentrations of Sky Blue and of SC_2 are 5.90×10^{-6} mol./l. and up to 1.20×10^{-4} mol./l., respectively. Curve I in the figure was drawn by making use of this value of K. It will be seen at once from the figure that the observed values (white circles) well fit the calculated curve; this means the formation of a 1:1 complex. If a 1:1 complex is formed, the curve of ΔD should show the same feature when the concentration of Sky Blue is varied, while that of SC_2 is kept constant, because of the symmetry of the equation. The curve of ΔD-concentration of Sky Blue is also shown in Fig. 5, where the black circles denote the observed values and curve II the calculated. These two also well fit each other within an experimental error. Therefore, the formation of a 1:1 complex of Sky Blue and SC_2 would well explain all the results obtained.

The absorption spectrum of the 1:1 complex of Sky Blue and SC_2 will, therefore, be obtained experimentally by making use of the equilibrium constant*.

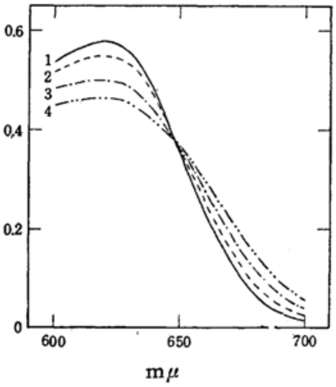

Fig. 4. Absorption spectra of mixtures of Sky Blue and SC_2 in aqueous solution at room temperature (30.5°C), where each absorption of SC_2 is subtracted from the corresponding mixture curve. 1 cm. cell. Concentration of SC_2 is 1: *zero*, 2: 6.08×10^{-6}, 3: 3.01×10^{-5} and 4: 1.20×10^{-4} mol./l. that of Sky Blue is 5.90×10^{-6} mol./l;

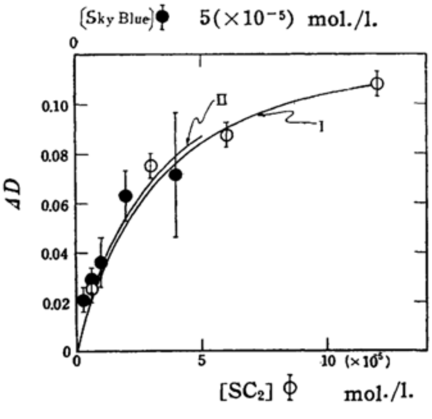

Fig. 5. The relation between the difference in density, ΔD, of the combination of Sky Blue with SC_2 and the concentration of SC_2 or of Sky Blue. 1 cm. cell, $\lambda=620$ mμ. $K=3.8\times10^4$ (at 30.5°C).
I: Calculated difference when the concentration of Sky Blue is constant (5.90×10^{-6} mol./l.); the white circles are corresponding observed values at 30.5°C.
II: Calculated difference when the concentration of SC_2 is constant (6.07×10^{-6} mol./l.); the black circles are representing observed values at 28.2°C.

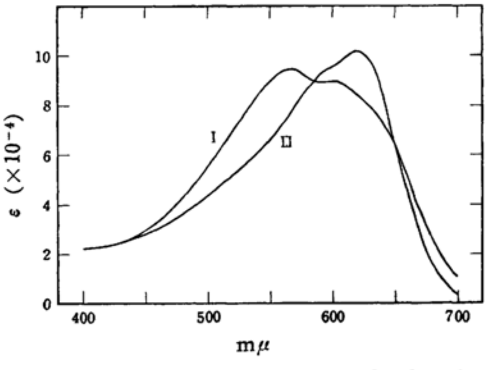

Fig. 6. Absorption spectrum of the 1:1 complex of Sky Blue and SC_2.
I: Complex
II: Sum of absorptions of the components (both 2.9×10^{-6} mol./l.)

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* If the equilibrium constant is known, the concentration of the complex corresponding to given amounts of the components can be calculated and then that of the components free from the complex formation will be known. Therefore, the absorption of the complex will be obtained by subtracting absorptions of the free components from that of the mixture.

The absorption spectrum of the complex (curve I) obtained from the experimental results shown in Fig. 3 is indicated in Fig. 6, together with the sum of those of the components (curve II). The figure shows clearly that the absorption of the complex is weaker in intensity than that indicated by the resultant curve at the first absorption band of Sky Blue (620mμ), but stronger at that of SC_2.

Discussion

It has been reported before¹⁾ that Sky Blue and certain monoazo acid dyes (*p*-nitroaniline → γ acid) form higher complexes richer in the acid dyes in presence of an excess of these dyes, when mixed in water⁴⁾. Though SC_1 and *p*-nitroaniline → γ acid are both monoazo acid dyes, only the former shows an isosbestic point in spectra when mixed with Sky Blue (Fig. 2). It seems that such a difference has relation to the fact that the substantivity of dyes increases with the length of the conjugated double bonds chain connecting their auxochromes⁵⁾, and that at the same time they come to associate with themselves easily⁶⁾.

According to measurements of the conductivity of SC_1 and $SC_2$⁶⁾, the association of SC_1 with itself is not noticed over a range of concentrations $(3\sim60)\times10^{-4}$ mol./l., while the formation of ion-micelles of SC_2 is clearly observed. From these results, Ando considered, according to the substantivity theory, that the length of the conjugated double bonds was closely related to the aggregation of SC_1 and SC_2**. It has also been known that, of dyes with various substituents, similar to Congo Red in constitution, those which have the stronger substantivity show the greater spectral change caused by their association³⁾. Therefore, though it is impossible to explain briefly the fact that a larger quantity is needed for SC_1 than for SC_2 to cause a change in spectrum when mixed with Sky Blue***, it may be said that this is partly due to the difference in the substantivity of SC_2 and of SC_1.

Derbyshire and Peters⁷⁾ obtained experimentally the absorption spectrum of a 1 : 1 complex of Sky Blue and Chrysophenine G. To be compared with the present result (Fig. 6, curve I), their spectra are shown in Fig. 7, in which curve I shows the absorption of the 1 : 1 complex and curve II the sum of those of the components. Inspection of these figures shows that the absorption of each mixture corresponding to the first band of the dye combined with Sky Blue shifts to longer wavelengths with an increase in intensity. On the other hand, the absorption corresponding to the peak of the first band of Sky Blue (620 mμ) shifts to longer wavelengths, with a peak getting more distinct, in the complex of Chrysophenine G, while it disappears in the complex of SC_2. Derbyshire and Peters⁷⁾ consider that Sky Blue and Chrysophenine G can approach in parallel with each other and form a complex, because while Sky Blue has its charged groups at the ends of the linear molecule, the corresponding groups of Chrysophenine G are near the centre, so the repulsion between them is small. On the other hand, if SC_2, which has its charged group at an end of the molecule, forms a complex in parallel with Sky Blue, it may be repelled by the charged groups of Sky Blue. The difference between the spectra of the two complexes and their stabilities may be related to the fact just mentioned. Further, the fact

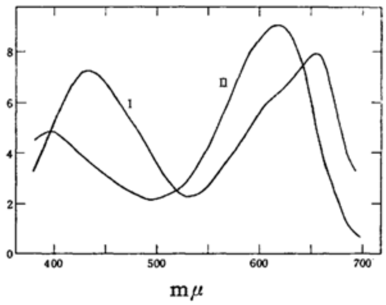

Fig. 7. Absorption spectrum of the 1 : 1 complex of Sky Blue and Chrysophenine G (quoted from the result of Derbyshire and Peters).

I: Complex

II: Sum of absorptions of the components

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[4] This fact has been recently confirmed by dyeing measurements from mixtures of the same pairs of dyes. [Y. Horiki, Y. Tanizaki and N. Ando, This Bulletin, to be published.]

[5] E. Schirm, *J. prakt. Chem.*, **144**, 69 (1935).

[6] N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **64**, 1305 (1943).

** The number of sulfonic groups per molecular weight of SC_2 is smaller than that of SC_1, and the former is more insoluble in water. This may be one of the reason why SC_2 more easily associates with itself.

*** If a complex is formed from two dyes, the extent of the change in spectrum of the mixture also depends on wavelengths of corresponding absorptions of the component dyes and the relative direction of their transitions (Ref. 2).

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

that the increasing order of length of the conjugated chain connecting the auxochromes is $SC_2 <$ Sky Blue $<$ Chrysophenine G may also be related to the difference between the spectra, according to the following reason. The first absorption band of a dye has close relation to the electron donating power of its auxochromes containing lone paired electrons[8], which are more easily affected by outer conditions than other π electrons under consideration. It will be seen that if both of the components approach in parallel with each other to form a complex, the auxochromes at both ends of Sky Blue get out of place from the π electron system of SC_2 or only one of them approaches it, though they draw near that of Chrysophenine G.

From the above discussion, it may be considered that the pair of Chrysophenine G and Sky Blue has a smaller intermolecular distance in a complex than that of SC_2 and Sky Blue. The amount of delocalization energy of π electrons between two components in a complex formed from molecules containing no lone pair electrons has been estimated[9]. If this idea can be applied to the present discussion, it will turn out that the pair of Chrysophenine G and Sky Blue is more stable than that of SC_2 and Sky Blue, and that the spectral change of the former is also larger; that is, in case of the former the electron transition corresponding to the first absorption band of Sky Blue will change more remarkably with larger intermolecular charge transfer (probably through auxochromes) than in case of the latter. Thus the character of the absorption spectra of the complexes can be explained qualitatively.

The above discussion will be applied to the difference between spectral characters of the pairs of SC_1 and Sky Blue and of SC_2 and Sky Blue.

Summary

1. The absorption spectra of the binary mixtures in aqueous solution of Chlorazol Sky Blue FF and sulfanilic acid → cresidine and sulfanilic acid → cresidine → cresidine were measured at room temperature.

2. The mixture of Chlorazol Sky Blue FF and sulfanilic acid → cresidine shows the additive spectrum when the ratio of the two dyes is about 1:5 but the non-additive one when it is about 1:40. From this fact the authors pointed out that even if an equimolar or nearly equimolar mixture shows the additive spectrum, it often exhibits the additive one with a relative increase of one component, due to the interaction between the components. That the spectra of the mixture pass through an isosbestic point means that a Sky Blue molecule interacts with n molecules of sulfanilic acid → cresidine (n is unknown).

3. It was indicated that the mixture of Chlorazol Sky Blue FF and sulfanilic acid → cresidine → cresidine showed the non-additive spectrum, and that this was well explained by assuming the formation of a 1:1 complex over the range of concentrations measured.

4. The authors discussed qualitatively the characters of the spectra and the stability of these complexes, comparing them with the complex of Sky Blue and Chrysophenine G, etc.

The intermediates used were presented by the Sumitomo Kagaku Kogyo Co. Ltd. through Dr. S. Arikawa and Dr. M. Okazaki. The authors wish to express their gratitude to them.

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[8] J. Tanaka and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 1200 (1957).
[9] K. E. Shuler, *J. Chem. Phys.*, **20**, 1865 (1952).