Absorption Spectra of Dyes. V[1]. *The Composition and Intermolecular Charge Transfer Spectra of Complexes Formed in Aqueous Solution of the Mixture of Chlorazol Sky Blue FF and Chrysophenine G*

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(Received December 2, 1959)

Most of the binary mixtures of dyes in aqueous solution studied before showed more or less non-additive spectra[1-6]. Of these dyes the pair of Chlorazol Sky Blue FF and Chrysophenine G revealed the most remarkable change in spectrum. This pair was first studied by Neale and Stringfellow[2], and then in more detail by Derbyshire and Peters[4]. According to the latter workers, only a 1 : 1 complex is formed between Chrysophenine G and Chlorazol Sky Blue FF in equimolar solution or in the presence of an excess of Chlorazol Sky Blue FF at room temperature, while higher complexes are formed to a certain extent in the presence of an excess of Chrysophenine G. However, they made no mention of the composition of these higher complexes. In the hope of obtaining some information about the composition of the higher complexes and then interpreting the spectral change observed on the basis of quantum chemical concept, this combination has been studied in greater detail.

A series of studies of binary mixtures of Chlorazol Sky Blue FF with some other dyes have shown that the relatively small spectral change observed in mixtures of some monoazo and disazo dyes may be explained by the perturbation between molecular orbitals of two component dyes caused by the formation of loose complexes[1,5]. However, it has been impossible to apply this concept to more compact complexes: a large spectral change which appeared in a binary mixture of Chlorazol Sky Blue FF has been unable to be explained without the concept of intermolecular charge transfer[1]. As the authors pointed out before, the mixture of Chlorazol Sky Blue FF and Chrysophenine G also shows a spectral change which implies the occurrence of charge transfer[1]. Therefore, this pair, which is considered to be a typical example of these sorts of dyes having the intermolecular charge transfer phenomenon, seems to be most suitable for our purpose.

1) Part IV of this series, T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 32, 680 (1959).
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).
5) Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, 32, 119 (1959).
6) T. Kobayashi, Y. Tanizaki and N. Ando, ibid., 32, 675 (1959).

Experimental

Preparation of Samples.—The purification of the dyes and the preparation of dye solutions followed the same methods as explained in the previous paper[1].

Absorption Spectra.—All the absorption spectra of dye solutions were measured by a Shimadzu QR-50 spectrophtometer at room temperature (27°~30°C). Cells used were 0.2, 0.5 and 1 cm. thick.

Hereafter Chlorazol Sky Blue FF and Chrysophenine G will shortly be called Blue (or B) and Yellow (or G), respectively.

Results and Discussion

1. The Composition of Complexes Formed in Solutions.—As is shown in Fig. 1, absorption spectra of mixtures of Blue and Yellow at

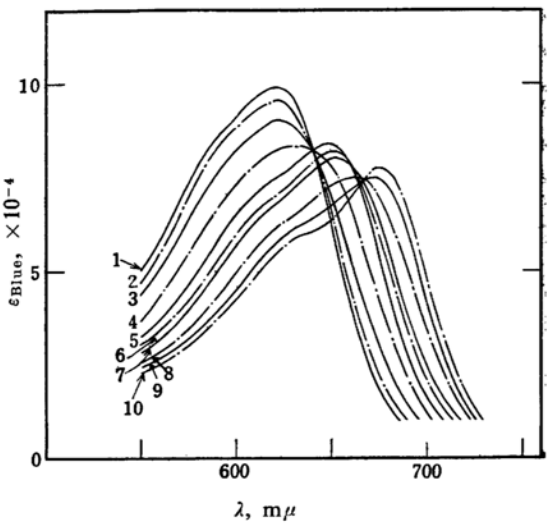


Fig. 1. Absorption spectra of mixtures of Blue and Yellow in aqueous solution at room temperature (ca. 27°C). The concentration of Blue is 1.00×10^{-5} mol./l. The ratio of the concentration of Yellow to that of Blue is 1-0, 2-0.105, 3-0.313, 4-0.610, 5-1.03, 6-1.55, 7-2.07, 8-4.18, 9-8.27 and 10-51.5.

wavelengths corresponding to the first absorption band of Blue (620 mμ) show a characteristic change, with an increase in the concentration of Yellow added into the solution containing a constant amount of Blue (1.00×10^{-5} mol./l.). It is already known[4] that, while the concentration of Yellow does not exceed that of Blue, spectra of mixtures of this pair have an isosbestic point at about 640 mμ accompanied with a new clear absorption band at 650 mμ. Fig. 1 clearly shows that, when the concentration of Yellow has increased more than four times as high as that of Blue, the second isosbestic point appears at about 670 mμ and 650 mμ band disappears, followed by the appearance of a new band at 675 mμ. Since Yellow does not absorb light in the wavelength region shown in the figure, these two isosbestic points mean that each molecule responsible for the 650 mμ band contains in itself one Blue molecule (the first isosbestic point), and that each molecule responsible for the 675 mμ band contains in itself one molecule of the complex (the second isosbestic point).

As has already been known, the 650 mμ band is due to a 1 : 1 complex[4]. Then, the molecular species of the 675 mμ band may be considered to be a complex made up of a 1 : 1 complex and Yellow in the ratio 1 : 1. Now, let us suppose that the molecular species which shows the 675 mμ band is a 1 : 2 complex richer in Yellow and that the following equilibriums exist in solutions.

$$B+G \rightleftarrows BG \qquad (K_1)$$

$$BG+G \rightleftarrows BG_2 \qquad (K_2)$$

It is possible to calculate the equilibrium constants (K_1 and K_2) corresponding to the above equilibriums, from observed obtical densities in accordance with the mass action law. They were calculated here by use of the difference ΔD between the sum of observed optical densities of the component dyes and the optical density of the corresponding mixture at 620 mμ, according to the usual method[3,6]. Since the observed optical density of the mixture is, in practice, the sum of those of the single dyes and the complexes, the calculation is complicated. Therefore, an approximate one was performed. As the figure shows clearly, the amount of 1 : 2 complex is negligibly small in the concentration region [B] > [G] (where [B] and [G] mean the initial concentrations of Blue and Yellow. respectively). Consequently, the value of K_1 was calculated from observed optical densities in the region [B] > [G]. The optical density at 620 mμ decreases with an increrase of [G], approaching to a certain value as [G] becomes large relative to [B]. This value may be considered to be due only to the 1 : 2 complex, BG_2. Thus the molecular extinction coefficient of BG_2 may be known, and by use of it, $K(=K_1K_2)$, the overall equilibrium constant of the formation of the complexes, may be calculated. K_2 can easily be obtained from K and K_1. Calculated values of K_1 and K_2 were about 6×10^5 and 5×10^4, respectively, at 27°C.

Now as the values of K_1 and K_2 were thus decided, the concentrations of BG and BG_2 corresponding to any amounts of Blue and Yellow will be obtained, according to mass action equations, hence the difference of optical densities ΔD will be calculated by use of them. Calculated $\Delta D\sim$ [G] curves when the initial concentration of Yellow is varied with that of Blue kept constant are shown by full lines in Fig. 2,

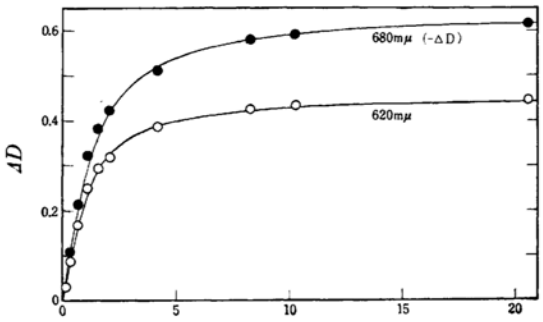


Fig. 2. The difference in optical densities when the concentration of Blue is constant (1.00×10^{-5} mol./l.) at 27°±1°C. 1 cm. thick.
Full lines: calculated differences
Black and white circles: observed differences corresponding to the respective curves

in which the lower and upper curves show the differencce at 620 mμ and at 680 mμ, respectively. The latter is described as $-\Delta D$ because it has negative values. Observed values corresponding to each curve are shown by white and black circles. They are coincident well with the respective calculated curves.

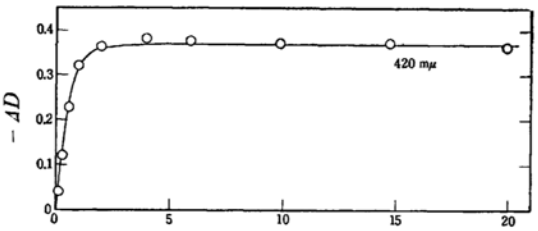


Fig. 3. The difference in optical densities when the concentration of Yellow is constant (1.00×10^{-5} mol./l.) at 28°±1°C. 1 cm. thick.
Full line: calculated difference
White circles: observed differences corresponding to the calculated curve

A corresponding calculation was then made at 420 mμ, the concentration of Yellow being kept constant. The result ($-\Delta D\sim$[B] curve) is shown by a full line in Fig. 3, in which the white circles are corresponding observed values. The coincidence between the observed and the calculated values is also satisfactory in this case.

As seen above, each of the $\Delta D\sim$[G] and the $\sim$[B] curves calculated by use of K_1 and K_2, of which values were obtained from the observed optical densities at 620 mμ, explains the observed values well. This satisfactory coincidence between the observed and the calculated values of ΔD means the propriety of the assumption that a 1:1 complex and a 1:2 complex are formed in equilibrium in the mixture solution. Further it affirms that the obtained values of K_1 and K_2 are proper.

Now, it has become clear that two sorts of complexes exist in the mixture solution, in addition to the component dyes. Therefore, the behavior of the spectral change shown in Fig. 1, i. e., the shift of the first absorption band from 620 mμ to 650 mμ and to 675 mμ through the two isosbestic points with an increase in concentration of yellow, may be expressed in the quantitative relation among these components and complexes. The consentrations of Blue and the two complexes change with an increase in amount of Yellow as shown in Fig. 4, in which Curves I, II and III show the concentrations of free Blue, BG and BG_2, respectively. As the figure shows, the existence of BG_2 is negligible when it is compared with the others, in the region where the amount of Yellow is less than 0.5×10^{-5} mol./l. Consequently the spectral change of the mixture will be governed only by the amounts of free Blue and BG (the first isosbestic point). When the concentration of Yellow is further increased, free Blue decreases to a nigligible amount, hence the spectral change is governed only by the amounts of BG and BG_2 (the second isosbestic point). Thus the change in spectra of the mixtures shown in Fig. 1 will well be understood through the relation between the concentrations of the components and the complexes shown in Fig. 4.

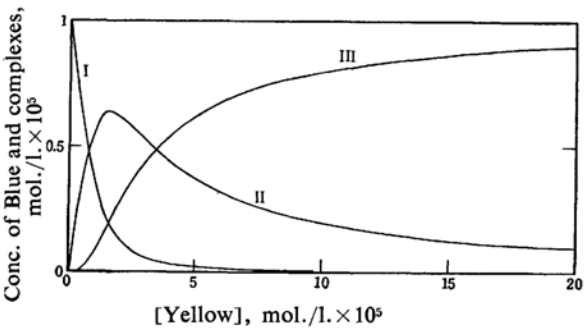


Fig. 4. The changes in concentrations of Blue and the complexes with that of Yellow when the initial concentration of Blue is 1.00×10^{-5} mol./l.
I: free Blue, II: BG, III: BG_2

2. The Change in Absorption Spectra.—The discussion in the previous section has clarified that a 1:1 complex BG and a 1:2 complex BG_2 are formed in aqueous solution of the mixture of Blue and Yellow. The equilibrium constants (K_1 and K_2) for these complexes have also been obtained. Therefore, absorption curves of the complexes can be drawn from observed absorption spectra of mixtures. The curves shown in Fig. 5 are the absorption spectra of BG and BG_2 thus obtained*. Inspection of the absorption spectra of the components and the complexes

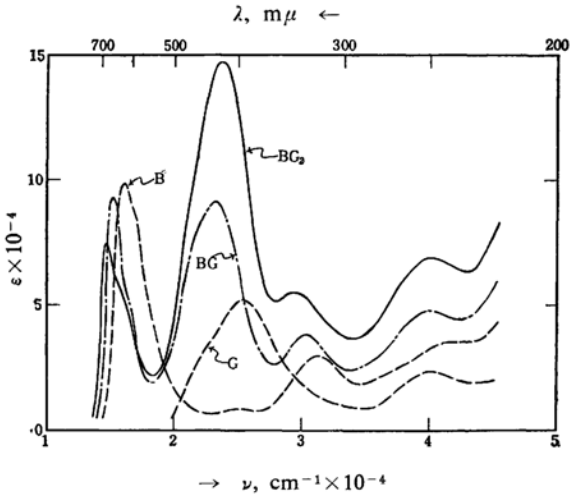


Fig. 5. Absorption spectra of the complexes and the component dyes

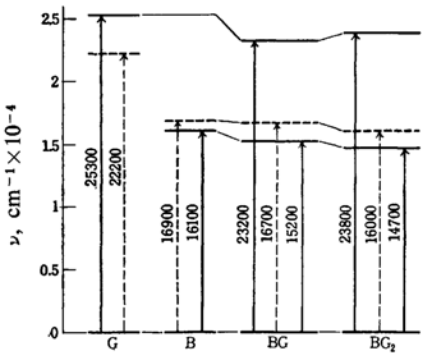


Fig. 6. Observed transition energies (cm^{-1}) of Yellow (G), Blue (B) and the complexes (BG and BG_2)

* Since these curves were made from absorption specra which were converted from those measured in various cells different in thickness so as to correspond to the unit cell, their molecular extinction coefficients and maximum wavelengths shown in the figure may have some errors.

shows that the first absorption bands shift to longer wavelengths with a change from Blue to BG_2; on the other hand, the absorption of BG corresponding to the first absorption band of Yellow (395 mμ) is markedly shifted to longer wavelengths (430 mμ) with a remarkable increase in intensity, while that of BG_2 to shorter wavelengths (420 mμ) than that of BG is. To show these changes more clearly, the transition energies (cm^{-1}) of Blue, Yellow, BG and BG_2 are given in Fig. 6, where the dotted lines mean absorptions corresponding to shoulders. The absorptions illustrated in Fig. 6 seem to show a regular change, except those in the shorter wavelength region, in view of the fact that they shift to longer wavelengths with a change from Blue to BG_2. The absorptions of the complexes in the shorter wavelength rigion seem to have an unusual behavior. Perhaps they are charge transfer spectra, as the following discussion will suggest.

The first absorption bands of dyes are generally considered to be due to conjugated double bond chains connected with auxochromes. According to the VB theory, the first absorption bands of Blue and Yellow may be considered to be owing to resonances between the following extreme structures.

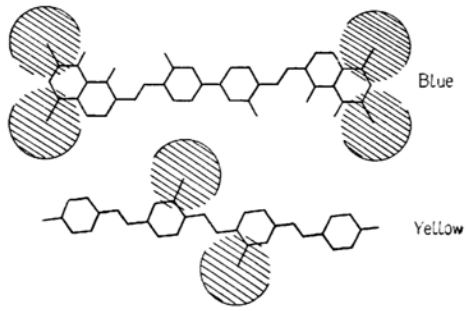
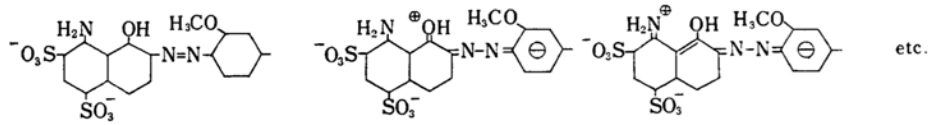
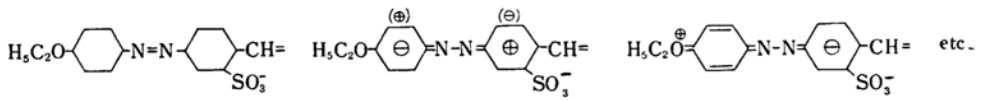


Fig. 7. Models of Blue and Yellow. The shadowed circles mean sulfonic groups.

pointed out before[4] and the structures in Fig. 7 show clearly, Blue and Yellow might approach close each other without accepting the repulsion of their charged groups, if they form complexes with their molecular axes in parallel with each other. In such structures, the auxochromes of Blue may have higher possibility of being covered by the conjugated system of their partners than those of Yellow, so unshared π-electrons of the auxochromes of Blue may be more affected than those of Yellow. These conditions may make the ground state of Blue unstable, the contribution of structure I to it



I II III



I′ II′ III′

where the half of the structure of each dye is shown. Though there are a number of extreme structures, they are lumped together under the structures of which inner π-electron systems have negative charge. The first absorption band of each dye may approximately be expressed by a transition from the ground state (mainly I or I′) to an excited state (mainly II or II′)**. As

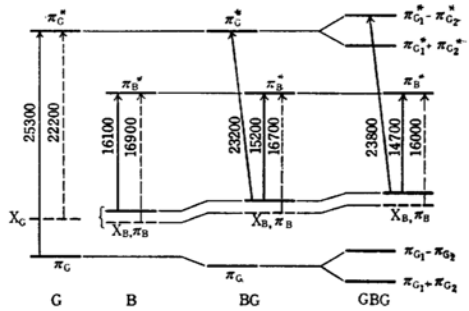
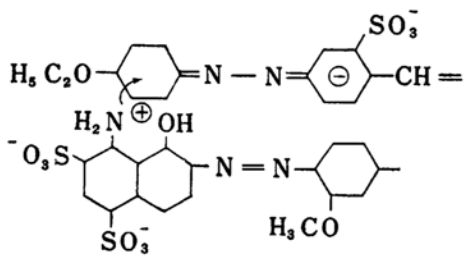


Fig. 8. Schematic representation of electronic transitions among molecular orbitals of Yellow (G), Blue (B) and the complexes (BG and GBG)

** According to empirical facts, auxochromes, which are attached to a naphthalene ring as a coupling component, show, in general, greater effects on absorption spectra, when attached to the inner ring having an azo group. Hence, the excited state of Blue seems to consist mainly of structure II. In case of Yellow, as the effect of OC_2H_5 as auxochrome seems to be weak because of its weak electron donating power relative to NH_2, ect.,[7] it may approximately be considered that the shoulder of the first absorption hand is due to the resonance I′↔III′ and the peak to I′↔II′.

7) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Orgnic Chemistry", Edward Arnold, London, (1957), p. 129.

smaller, and, at the same time, charge transfer from Blue to Yellow easy. The important structure of an excited state in this case may be



in which a mobile electron of Blue in structure II or III transfers to the inner π-electron system of Yellow***.

The same discussion will be given on BG_2. The structure of BG_2 may be considered to be a sandwich type with B in its inside. The two G molecules in this complex are supposed to be close to each other in spite of holding B between them, so it is necessary to take into account an interaction between them: the mixing may occur to some extent between the excited states of G molecules, causing them to split in two different levels. The experimental results suggest that the charge transfer from B may occur to the higher level, though it can not possibly be ascertained.

According to the MO method, the spectral change will be explained as follows. A rough approximation shows that the first absorption bands of the dyes are due to electron transitions of unshared π-electrons of the auxochromes to the lowest vacant orbitals of the inner π-electron systems, i. e., the $X \rightarrow \pi^*$ transitions in Fig. 8****. In case of Yellow (G), this is $X_G \rightarrow \pi_G^*$. As the electron donating power of OC_2H_5 is weak relative to that of NH_2[7], howerver, this absorption may also be weak. Probably the principal absorption band of G is due to $\pi_G \rightarrow \pi_G^*$. In case of Blue, it is difficult to know which auxochrome X_B corresponds to, because Blue has many auxochromes. Consequently, they are lumped together under X_B.

If Bule and Yellow from the complex BG with the structure mentioned above, the first probable change will arise between π_G and X_B (and π_B), because the auxochromes of B may be affected strongly by the inner π-electron system of G; a repulsion between these MO's will occur to make such a pattern as BG in Fig. 8. It was supposed here that no interaction happens between π_B^* and π_G^*. If a geometrical arrangement of the orbitals X_B and π_G^* in the complex is taken into consideration, the $X_B \rightarrow \pi_G^*$ transition, i. e., an intermoleculer charge transfer, may be expected to occur easily.

Concerning the complex BG_2, as already mentioned, its structure may be as GBG, with the linear molecules standing side by side. Since the G molecules stand close to each other in spite of B existing between them and parallel with each other, the complex has at least one symmetry. Consequently, the two π_G^* orbitals mix to separate into $\pi^*_{G_1} + \pi^*_{G_2}$ and $\pi^*_{G_1} - \pi^*_{G_2}$. As seen in the discussion based on the VB theory, it is also difficult to ascertain to which molecular orbital the charge transfer from B occurs. The experimental results, however, mean that it may be $X_B \rightarrow (\pi^*_{G_1} - \pi^*_{G_2})$. On the other hand, it is clear from the above discussion that the X_B level in GBG is pushed up higher than the one in BG.

Though there is no ground for justifying the relative positions of the molecular orbitals in Fig. 8, the spectral changes shown in Fig. 6 could be explained at least qualitatively by the above discussion based on the MO method. Some parts of the above two discussions were not always perfect, but it should be noted that the spectra of the complexes could not be explained without the concept of charge transfer. Explanation of these specteal changes by a solvent effect caused by the close approach of dye molecules was attempted, without considering the charge transfer, only to fail; the first absorption band of Yellow was insensitive to the change in pH or in solvent. So, it follows that the strong absorptions at about 420 mμ of the complexes can not be explained by a mere solvent effect.

Thus the absorption spectra of the complexes formed of Blue and Yellow could be explained qualitatively on the basis of those of the components. A binary mixture of Blue, in which the formation of a 1 : 1 complex is proved, also showed a change in spectrum which might not be explained without the concept of charge transfer.[1],***** It cannot always be said, however, that its charge transfer occurs in the same mechanism as is considered in the present work. The main reason will be found in the fact that the partner of Blue has no such symmetry in its structure as Yellow has and that the obvious factors suggesting the arrangement of the component dyes in the complex are not found.

*** Since the amino groups have less effect on the spectrum of Blue than the hydroxyl groups and the electron donating power of the former is stronger than that of the latter, as mentioned in footnote 2, an electron of one of the amino groups may be considered to have high possibility of acting in the intermolecular charge transfer. However, it is impossible and unnecessary to confirm the fact.

**** X and π mean the orbital of unshared electrons and the inner π-orbital, respectively.

***** Blue and Durazol Red 2B forms a 1 : 1 complex in aqueous solution (see Ref. 3), of which spectrum seems not to be understood without considering charge transfer.

Summary

1. The change in absorption spectra of mixtures of Chlorazol Sky Blue FF and Chrysophenine G in aqueous solution was stoichiometrically studied in detail and a 1 : 1 complex and a 1 : 2 complex were proved to be formed.

2. The absorption spectra of the complexes were drawn from experimental results by use of the calculated equilibrium constants, and the phenomena of these absorptions were qualitatively explained according to VB and MO methods, with the conclusion that charge transfer spectra from Chlorazol Sky Blue FF to Chrysophenine G appear in the complexes.

The authors wish to express their thanks to Professor Ikuzo Tanaka for his helpful discussion.

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