Absorption Spectra of Dyes. II[1]. *On Non-additivity of Absorption Spectra of Binary Mixtures of a Direct Dye and Some Acid Dyes in Aqueous Solution**

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It has been known that absorption spectra of binary mixtures of dyes in aqueous solution are not always additive[2,3] probably owing to the formation of complexes between dyes in solution, and it is also well known that in dyeing from solutions of mixtures of two dyes, the amounts of dyes adsorbed are frequently non-additive (i. e. a reduction in adsorption)[3]. Moreover in such cases, it seems that there exist some relations between non-additive properties in the amounts of dyes adsorbed and those in absorption spectra. In practical dyeing, mixtures are more frequently used than a single dye in order to produce any desired shade, so that the scientific study on dye mixtures is not only interesting from the physicochemical point of view, but also important practically. For this reason, in our laboratory, the investigation about dye mixtures has been started and the attention is first focused on non-additivity in spectrum.

Hitherto, only a few studies on non-additivity in absorption spectrum of dye mixtures have been carried out[2,3]. Neale and Stringfellow[3] showed that the mixture of Chlorazol Sky Blue FF and an acid dye (*o*-anisidine → H acid) shows non-additive property in absorption spectra, while the mixture of Chlorazol Sky Blue FF and Orange II has an additive spectrum. In this paper, selecting several monoazo acid dyes, the formula of which can be expressed *p*-X-aniline → γ acid with different substituents X, the authors investigated the spectra of pairs of Chlorazol Sky Blue FF and these acid dyes, ranging over the visible and near ultraviolet regions, and found that all of them were more or less different from the sum of the corresponding spectra of their components.

In this paper, a qualitative explanation of non-additivity in spectrum of such mixtures will be given by means of the conventional quantum chemical concept.

Experimental

Materials.—Direct Sky Blue 6B of Mitsubishi-Kasei Co., Ltd. was used as the sample of Chlorazol Sky Blue FF and it was purified by the usual method of Robinson and Mills[4], and the acid dyes made by coupling diazotized *p*-X-aniline with γ acid in acid or alkali solution, were purified by the same method.

Preparation of Samples.—Conductivity water of about 3.5×10^{-7} mho at room temperature was used for the preparation of dye solutions. The

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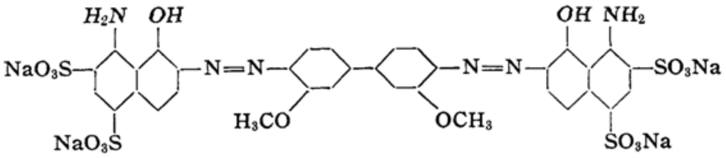
[1] Part I of this series, Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 343 (1957).

* Presented at the 11th Annual Meeting of the Chemical Society of Japan, April 1958.

[2] D. R. Lemin and T. Vickersraff, *Trans. Faraday Soc.* **43**, 491 (1947); A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers Col.*, **72**, 268 (1956).

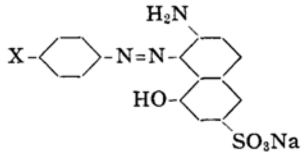
[3] S. M. Neale and W. A. Stringfellow, ibid., **59**, 241 (1943).

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

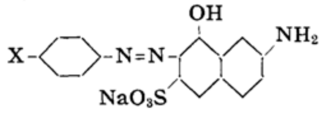


concentrations were 3.59×10^{-6} moles/liter and $1.78\sim1.81\times10^{-5}$ moles/liter for Direct Sky Blue 6B and acid dyes, respectively; these concentrations were determined by the fact that the change in spectrum was the largest when the ratio was about 1 : 5[5].

Dye samples will be conveniently abbreviated in this paper as follows: Direct Sky Blue 6B will be referred to briefly as "Sky Blue". And monoazo acid dyes (*p*-X-aniline → γ acid)



(I) (X-α)



(II) (X-β)

will be represented by substituents X, which means here H, CH_3, OCH_3, Cl and NO_2, of diazotized components and their coupling positions α or β; namely dyes of I will be briefly called X-α, or H-α, CH_3-α, etc. according to their substituents, and similarly those of II will be called X-β or H-β, CH_3-β, etc.

Measurements of Absorption Spectra.—For measurements of absorption spectra of dye solutions, the Shimadzu QB-50 and QR-50 spectrophotometers were used at room temperature (14° to 16°C). Absorption cells were 1 cm. and 2 cm. thick, and optical densities are always reduced to values corresponding to 1 cm. thick.

Results

The most marked non-additivity in absorption spectrum was found for the pair, Sky Blue and the acid dye with substituent NO_2, and in the case of Sky Blue and the acid dye with H for X the least non-additivity was found. As examples, spectra of the combinations of Sky Blue with NO_2-α and NO_2-β, whose non-additivity is the most remarkable, are shown in Figs. 1 and 2, respectively, with those of the components. In each figure curves I and II show the observed absorption curves of Sky Blue and the acid dye, respectively, curve III the sum of them, and curve IV the observed curve of the mixture. The difference, ΔD, between the sum of optical densities of its components and the observed one of a mixture is the largest in the neighborhood of a wave length of the principal band of Sky Blue (~620 mμ). And here, it is of interest that the bands corresponding to those of NO_2-β in the range of 400~460 mμ ($25\sim22\times10^3$ cm^{-1}) are additive, and that

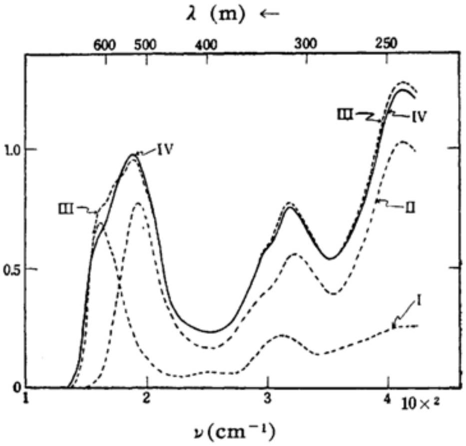


Fig. 1. Absorption spectra of a mixture of Sky Blue and NO_2-α, and its components. Curves I and II show the absorption spectra of Sky Blue and NO_2-α, respectively, curve III shows the resultant of curves I and II, and curve IV observed of the mixture.

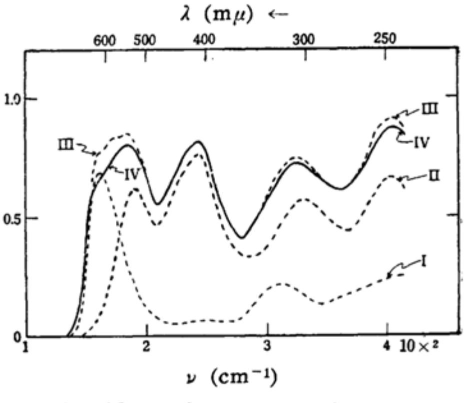


Fig. 2. Absorption spectra of a mixture of Sky Blue and NO_2-β, and its components. Curves show just the same case as in Fig. 1.

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[5] T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, to be published.

at the position corresponding to the first band of NO_2-α (~530 mμ) the observed absorption is more intense than the resultant one.

Now, observed wave numbers of absorption maxima of each component are shown in Fig. 3, in which values of difference ΔD between maximum densities of the resultant curve and those of the observed one of a mixture are also shown in round brackets at corresponding positions of absorption bands of acid dyes. Values of ΔD at the principal band of Sky Blue (161×10^2 cm^{-1}), however, are shown in the lowest line corresponding to each acid dye component. Fig. 3 shows distinctive facts to be summarized as follows.

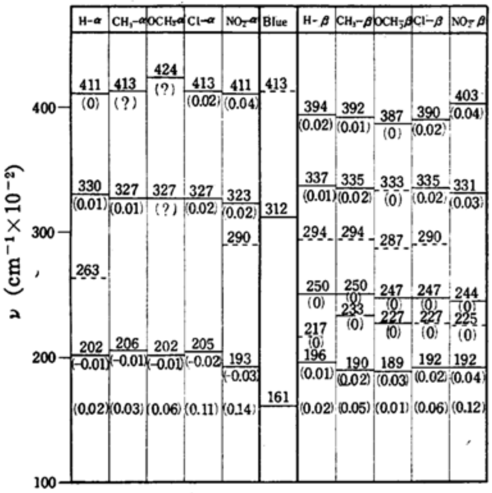

Fig. 3. Observed wave numbers of absorption bands of component dyes. Full and dotted lines mean the maximum positions and shoulders, respectively. Numbers in brackets show the difference between maximum optical densities of the sum of component spectra and observed ones of mixtures.

(1) It can be seen that non-additivity of absorption spectra appears in such positions that the absorption maxima of each component of a mixture are close to each other and there appears such a tendency as that the smaller the difference in wave number between them the larger the difference ΔD.

(2) The observed density near the position corresponding to a wavelength of the first band of each acid dye is smaller than the resultant in the case of Sky Blue and X-β, while it is larger when the acid dye component is X-α, that is to say, ΔD has the negative sign in the latter case.

(3) Absorption bands of the combination with X-β show the additive property in the region of $22\sim25\times10^3$ cm^{-1} (460~400 mμ).

(4) Every mixture shows the largest ΔD at the position corresponding to the wavelength of the principal band of Sky Blue.

Discussion

It may be supposed that such non-additivity in a spectrum comes from the formation of so loose complexes in a solution of dye mixture that the intermolecular charge-transfer does not occur, but some interaction between energy levels of components probably appears provided that their energies are close by. In such a case, for instance, when the excited levels A and B responsible for the absorptions of component dye molecules of a complex interact slightly with each other, it would be assumed that the absorption bands due to the individual transitions change only in wave number, not changing approximately in shape and intensity. Thus, if the spatial configuration of two molecular species were settled, the magnitude of the perturbation would naturally depend upon the difference between energies of A and B, the relative orientation of them in complex or the respective oscillator strength. But if it could be regarded that the effects of the latter two factors were not large and were the same in any complex considered here, the difference between the energies of excited states would become the main factor; namely, the nearer the energies, the larger the perturbation. According to the above consideration, the change in the spectrum of the complex may be approximately discussed by only the difference

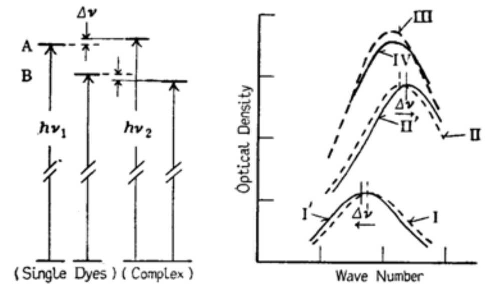

Fig. 4. A schematic illustration of the spectral change in a loose complex. Absorption curves are drawn with a shift of 200 cm^{-1} of each band of the component to the opposite side.

in wave numbers of the corresponding absorption bands of the components. In Fig. 4 the relation between the absorption band of a mixture and those of its components are shown schematically*. In this figure, curves I and II are the absorption bands of the components before interacting, curves I′ and II′ are those after interacting, and curves III and IV are the sums of curves I and II and of curves I′ and II′, respectively. The figure indicates that the intensity of the absorption band composed of those of components after interacting is always smaller than that composed of those before. From studies of dichroism for such dyes as used here, it could be regarded that an apparent single band in the ultraviolet region is the superposition of two, of which the directions of oscillation are orthogonal to each other, originated from the aromatic nucleus of the complicated coupling component[6]. And for this case an explanatory figure also might be given. For example, instead of A mentioned above, $A_{\parallel}$ and $A_{\perp}$ which are orthogonal and close in energy to each other might be considered and the following cases should occur. According to whether $A_{\parallel}$ is directed parallel, normal or inclined to $B_{\parallel}$, the resulting curves will become somewhat different in shape. But practically, the main features of drawn curves for respective cases showed a similar tendency as shown in Fig. 4, indicating a decrease in intensity of the curve after interacting. Anyway, a qualitative and reasonable illustration thus can be obtained for ΔD described in (1) in the foregoing section.

Quite similarly the above consideration will be applied to explain the difference ΔD between the sum of densities of Sky Blue and X-β and the observed one of the mixture at the position corresponding to the first band of X-β. This band is perhaps due to a single absorption and could interact with the first band of Sky Blue in complexes. On the other hand, when a component is X-α the corresponding ΔD has the negative sign. This can be explained, however, if it may be assumed that the first band of X-α consists of two absorption bands, of which one has the same property as the first band of X-β and the other has the different. This assumption is based on the evidence from the dichroic measurement of such dyes in stretched polyvinyl alcohol-sheet[7]. Dichroic properties of some of the dyes used are shown in Fig. 5, in which the curves show absorption spectra when the direction of the electric vector of incident polarized light coincided with the stretch direction. These suggest that respective bands in each curve connected by dotted lines would correspond to each other[7]. It is now possible to assume that the band of the longer wavelength side of two subsidiary bands composing the main band of X-α corresponds to the first band of X-β and is able to interact with the first band of Sky Blue, while the other band of the shorter side has less or no interaction with that of Sky Blue. On the other hand, in Fig. 1 or 2, in which the shoulder of the first band of component Sky Blue (~580 mμ) becomes more distinctive in the

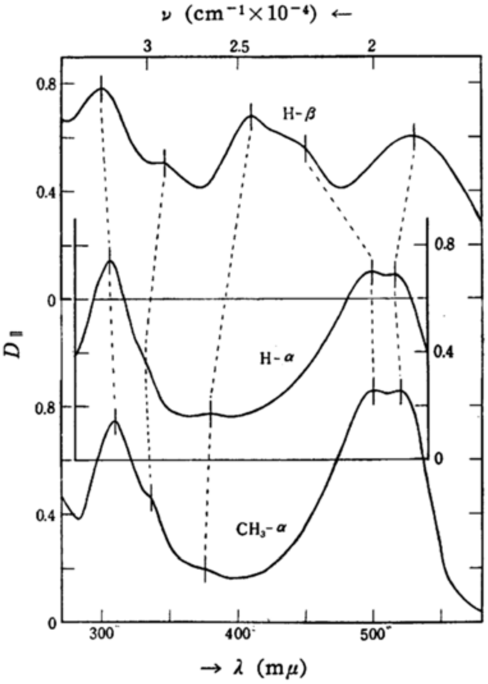

Fig. 5. Absorption spectra for plane polarized light of H-α, CH_3-α and H-β in stretched polyvinyl alcohol sheets when the stretch direction is parallel to the electric vector of incident polarized light.

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* The polarizability of such a molecule used here may be more responsible for its excited states than the ground state. Therefore, in a complex the interaction between the excited states of the components may be larger than that between the ground states. In Fig. 4, in order to discuss the relative change in levels, all the ground states are indicated on the same line.

6) Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 542 (1957).

7) Y. Tanizaki, presented at the 9th Annual Meeting of the Chemical Society of Japan, April 1956.

resultant curve, it may be presumed that the main absorption band of Sky Blue also consists of such two bands as those just mentioned for X-α. Further the subsidiary band of the longer wavelength side of Sky Blue seems to be more sensitive to the change in external condition than that of the shorter side[8]. Consequently, the correlation shown in Fig. 4 may be able to be diverted by the following method to illustrate the facts described in 2 and 4 in the last section, that is, values of ΔD, near the wavelengths of the first bands of the acid dyes, have the positive sign for pairs of Sky Blue and X-β but the negative sign for those of Sky Blue and X-α, and the largest value is found at the wavelength of the principal band of Sky Blue. If it is supposed schematically that the first absorption band of an X-α consists of two bands shown by curves I′ and II′ in Fig. 4 and is expressed by curve IV, it will be changed to curve III, after being perturbed, with the relative shift of the just-mentioned two bands composing it, while for Sky Blue the reverse is the case; that is, curve III means the principal band of Sky Blue before being perturbed and curve IV that after being perturbed.

Now, supposing that the bands of the shorter wavelength side shown by curves I_b and II_b in Fig. 6, which are constituents of the first bands of Sky Blue (I) and NO_2-α (II), respectively, would remain unchanged, and only the bands of the longer side, curves I_a and II_a, interact with each other, there can be obtained curve IV which, corresponding to the observed absorption, is the resultant of the new component bands coming from the shift just mentioned ($I_a \rightarrow I_a'$, $II_a \rightarrow II_a'$). And curve III shows the sum of curves I and II. The case of the mixture of Sky Blue and NO_2-β is shown in Fig. 7, in which the band of NO_2-β indicated by curve II is assumed to be a single band. In these figures the resolution of the main band into subsidiary bands has been properly made. The curve IV in each figure shows the coincidence in character with those observed (see Figs. 1 and 2). In Fig. 7 it is seen that curve IV is also stronger in intensity near a wave number of 20×10^3 cm^{-1} than curve III; in fact observed results showed, though not very clearly, such a tendency.

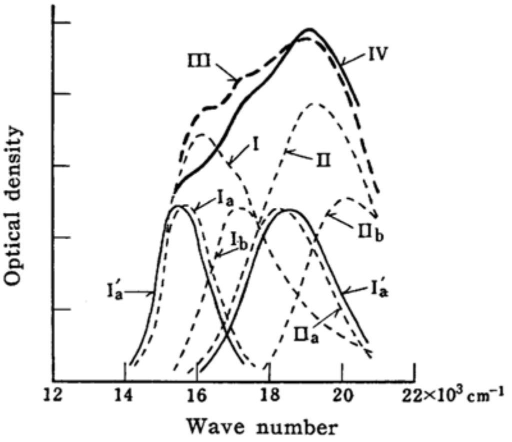

Fig. 6. Absorption curves of a mixture of Sky Blue and NO_2-α, before and after interacting, of the first bands. It is assumed that the interaction occurs only between the bands in the low wave number side, each of which shows a shift of 200 cm^{-1}.

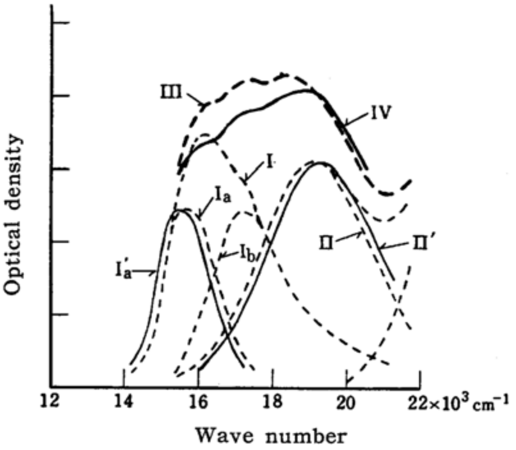

Fig. 7. Absorption curves of a mixture of Sky Blue and NO_2-β, before and after interacting, of the first bands. It is assumed that the interaction occurs between the first band of NO_2-β, which is a single band, and the band of the low wave number side of Sky Blue, each of which shows a shift of 200 cm^{-1}.

It was assumed above that the band of the shorter wavelength side of two constituents of the first band of X-α has less or no interaction with the main band of Sky Blue, corresponding to the second band of X-β (see Fig. 5). If it is true, the second band of X-β should show the

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[8] Y. Horiki, unpublished. For example, the maximum wavelengths of the first band of Sky Blue in water and in water-pyridine (20% for pyridine) solution were 618 mμ and 630 mμ, respectively, indicating the shift $\Delta\nu =$ 310 cm^{-1}. On the other hand, though the determination for the convex parts was not so accurate, it seemed that $\Delta\nu$ was smaller than 290 cm^{-1}, and the shoulder was more distinctive in pyriditine solution than in water.

additive spectrum in the combination with Sky Blue. The results observed are indeed in agreement with this expectation. At the same time, the third band also shows the additive property as shown in Figs. 2 and 3. Consequently, it might be considered another reason for the fact described in 3 in the last section that even the band of Sky Blue nearest to the X-β band under consideration lies too far apart for them to interact with each other.

It is well known that the first absorption band of such a dye as used here is quite generally ascribed to the electronic oscillation along the longest conjugated system which includes, as terminal groups, auxochromes characterized by lone-paired electrons in them. That is, the excited state is produced by the migration of an electron on such a terminal group to the inner π-electron system. On the other hand, such frontier electrons may be less protected from the change in the external condition, and are therefore affected easily. It may be, therefore, considered that the first band is more sensitive to the external change than the other bands. Thus, this may be followed by the fact described in (4) in the foregoing section that every mixture shows the largest ΔD at the position corresponding to the principal band of Sky Blue.

Finally, it is interesting to note that ΔD is the largest when X is NO_2 and the smallest when X is H (see Fig. 3). This might be related to the difference in nature of substituents X, but at present there could be found no interpretation for it from these qualitative investigations. As an empirical fact, it can be said that in order to investigate complexes formed in binary mixtures of Sky Blue and the acid dyes used here, NO_2-α or -β will be the most suitable to be selected.

Summary

1. Absorption spectra of mixtures of Direct Sky Blue 6B with *p*-X-aniline $\rightarrow \gamma$ acid, in which the substituent X means H, CH_3, OCH_3, Cl or NO_2, and the components in aqueous solution were observed in the visible and near ultraviolet regions.

2. All the absorption bands showed non-additive property, excepting the bands in the region of 400~460 mμ of the mixtures of Sky Blue and X-β shown in Figs. 2 and 3. And optical densities of observed bands of a mixture were generally smaller than sums of the values of each component, but when the acid dyes made by α coupling were used as other components, increases were seen at the positions corresponding to wave lengths of the first bands of them.

3. An explanation for these non-additive properties was given by means of the interaction between the corresponding bands of components.

4. At the same time, in this connection, it is pointed out that the apparent single band of the first of *p*-X-aniline $\rightarrow \gamma$ acid in α coupling consists of two bands and similarly the first band of Direct Sky Blue 6B may also consist of two bands.

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