Absorption Spectra of Dyes. VII[1]. *Some Steric Effects and Auxochrome-Effects on Complex Formation*[*1]

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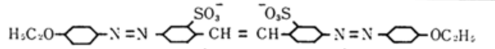
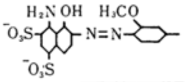
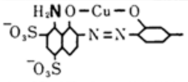
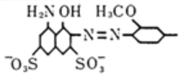
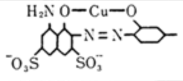
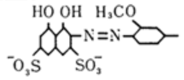
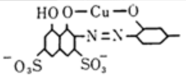
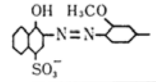
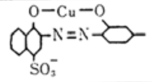
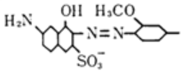
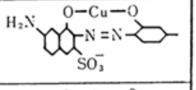
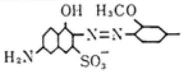
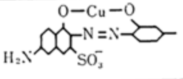
The interaction between molecules of different kinds of dyes in aqueous solutions has been studied extensively[2-4]. This problem is especially interesting because the forces involved in the complex formation are considered to be closely related to those responsible for the combination of dye molecules or ions with cellulose[2,3]. According to the conventional theory of the substantivity of dyes, it is important for substantivity that the molecule be planar so as to maintain a conjugated system between the terminal auxochromes, and that the hydrogen bonding be capable of being formed between such auxochromes and functional groups of cellulose. As for the latter, no direct experimental evidence has yet been obtained, though the possibility of hydrogen bonding between dyes and cellulose seems to be great. Nevertheless, there is no doubt that the auxochromes, by their functional property, play an essntial role in the formation of the complex or in the adsorption on cellulose.

In the present investigation, in order to obtain some preliminary information on how the above two factors, i.e., the steric effect by which the planarity of the dye molecule is hindered and the effect of the auxochromes, are reflected in the 1:1 complex formation, we examined the spectral changes of the binary mixtures of dyes described in the preceding paper[1], with Chrysophenine G as the common ingredient.

TABLE I. THE CHEMICAL STRUCTURE OF CHRYSOPHENINE G AND HALF CHEMICAL STRUCTURES OF DYES USED AND THEIR NOTATIONS



G (Chrysophenine G)

Notation	Half chem. structure	Notation	Half chem. structure
2S		2S(Cu)	
H		H(Cu)	
Ch		Ch(Cu)	
NW		NW(Cu)	
γ		γ(Cu)	
J		J(Cu)	

Experimental

Sample.—The dyes used are shown by notations in Table I, with the drawings of their half structures, except for Chrysophenine G, a full-structure drawing is given. Since all the dyes but Chrysophenine G differ only in their coupling components, for convenience let us call them by abbreviations such as 2S or NW taken from the name of the coupling components. Corresponding copper derivatives will also be called 2S(Cu), NW(Cu), etc. The J dye was prepared by coupling diazotized J acid with dianisidine, and J(Cu) was obtained from the J dye and copper sulfate by the usual method[5]. The other dyes were the same as those used before[1].

Absorption Spectra.—Most absorption spectra were measured with a Shimadzu QR-50 spectrophotometer at room temperature (21±3°C); the spectra of only the mixture of J and G (Chrysophenine G) were recorded with a Hitachi EPS-2 recording spectrophotometer. The other experimental procedures followed have already been reported[1,4),*3].

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[1] Part VI of this series: T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 33, 913 (1960).

[*1] Presented at the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

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[2] M. N. Inscoe, J. H. Gould, M. E. Corning and W. R. Brode, *J. Research National Bureau of Standards*, 60, 65 (1958).

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

[4] T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 33, 661 (1960).

[5] U. S. Pat. 2036159 (1935).

[*3] Precautions were taken with light in order to avoid the phototropism of Chrysophenine G.

Results

In the dyes containing no copper a similar change against the G concentration was seen in the difference between the sum of the individual absorption curves and those observed with the mixed system, as seen in 2S (Sky Blue) and G[4]. Examples are illustrated in Figs. 1 and 2 for the mixtures of the Ch dye or of the NW dye and G respectively. Two well-defined isosbestic points appear, indicating the formation of two sorts of complexes, a 1 : 1 and a 1 : 2 complex. As seen from the first isosbestic point shown in Figs. 1 and 2, the molar ratio in the complex formed is 1 : 1 when the amount of G is not over the concentration of the partner dye. An equilibrium constant *K* for the formation of a 1 : 1 complex can be determined by the method mentioned elsewhere with the condition that the formation of a 1 : 2 complex is extremely small[4]. The *K* values thus determined for the 1 : 1 complex formation are listed in Table II[*4].

Figure 3 illustrates the absorption spectra (solid lines) in an aqueous solution of nearly equimolar mixtures (ca. 1×10^{-5} mol./l.) of G and second components not containing copper. The broken lines in the figure indicate the results of the individual curves of the components,

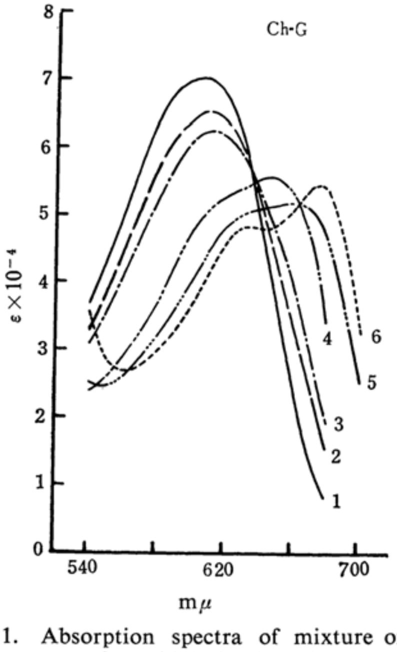

Fig. 1. Absorption spectra of mixture of Ch (chromotropic acid-derivative dye) and G (Chrysophenine G) in aqueous solution at room temperature.
ε : Absorption coefficient for Ch. ; Concentration of Ch : $1.20\sim1.24\times10^{-5}$ mol./l., Concentration ratio G/Ch : Curve 1 : 0, 2 : 0.25, 3 : 0.87, 4 : 8.2, 5 : 20, 6 : 82.4.

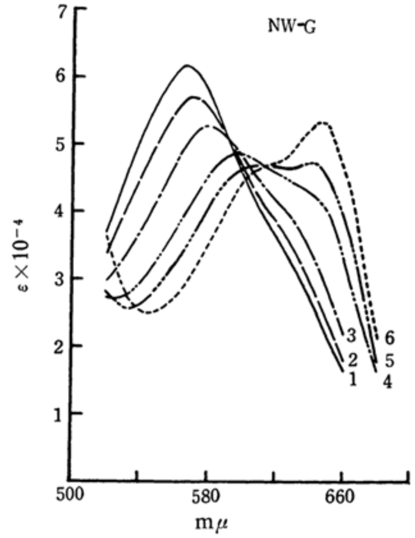

Fig. 2. Absorption spectra of mixture of NW (NW-acid-derivative dye) and G in aqueous solution at room temperature.
ε : Absorption coefficient for NW ; Concentration of NW : $1.00\sim1.04\times10^{-5}$ mol./l., Concentration ratio G/NW : Curve 1 : 0, 2 : 0.63 3 : 1.98, 4 : 4.24, 5 : 7.32, 6 : 19.2

TABLE II. THE CHANGE IN SPECTRA OF MIXTURES OF CHRYSOPHENINE G AND BENZIDINE DISAZO DYES IN AQUEOUS SOLUTION AT ROOM TEMPERATURE

Partner of G dye	Equilibrium constant *K* for 1 : 1 complex	$\Delta\nu$, cm^{-1} (*1)	$\Delta D/D$, % (*2)	Concn. (mol./l. $\times10^5$) (*3)
2S	6.0×10^5	2200	30	0.996 (1.009)
H	3.5×10^5	1400	19	1.067 (1.035)
NW	9.4×10^4	1600	26	1.060 (1.044)
Ch	7.7×10^4	1600	23	1.010 (1.058)
γ	3.7×10^4	1100	9	1.074 (1.007)
J	1.7×10^4	800	7	0.991 (0.999)

*1) Difference in wave number between maximum positions (around 400 mμ) of the sum and mixture curves, corresponding to the first absorption band of G alone : $(\nu_{\mathrm{sum}}-\nu_{\mathrm{mix}})$

*2) Decreasing ratio in optical density of the mixed system at the first maximum position (around 600 mμ) of the sum curve : $(D_{\mathrm{sum}}-D_{\mathrm{mix}})/D_{\mathrm{sum}}$, %

*3) The figure in parenthesis indicates the concentration of G dye combined.

[*4] Four to seven different concentrations of G were used in each mixture. The relation of the difference in optical density ΔD to G-concentration[4] was fairly well in agreement with the curve calculated with the respective *K* in Table II.

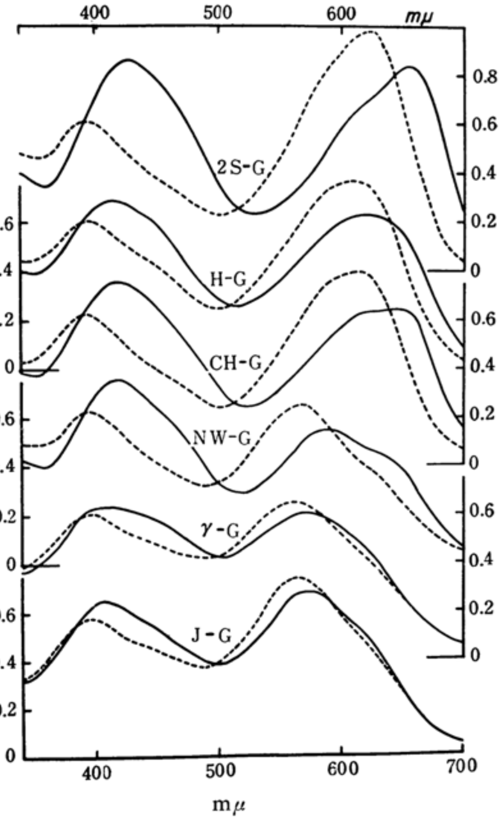

Fig. 3. Absorption spectra in aqueous solution of nearly equimolar mixtures of G and the second components (ca. 1×10^{-5} mol./l. each).
Solid line; observed with the mixture.
Broken line; resultant curve of the individuals of the mixture.

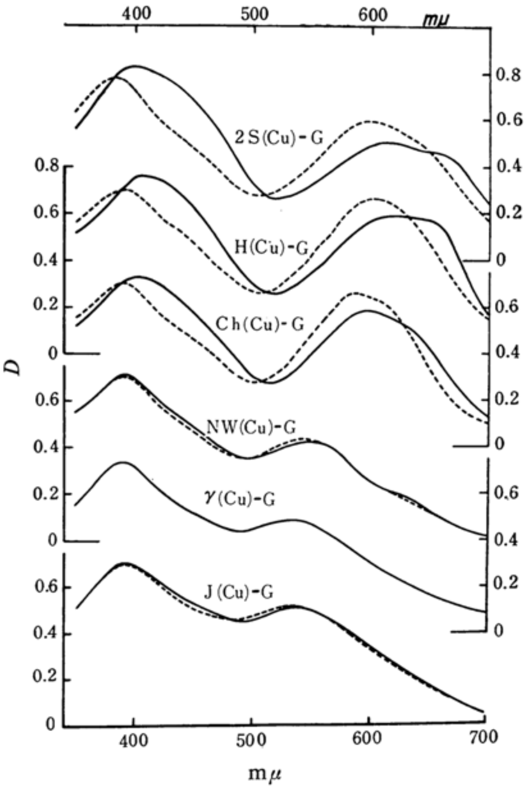

Fig. 4. Absorption spectra of mixtures of copper derivatives and the G dye (ca. 1×10^{-5} mol./l. each).
Solid line; observed with the mixture.
Broken line; resultant curve of the individuals of the mixture.

TABLE III. THE CHANGE IN SPECTRA OF MIXTURES OF CHRYSOPHENINE G AND COPPER DERIVATIVES IN AQUEOUS SOLUTION AT ROOM TEMPERATURE

Partner of G dye	$\Delta\nu$, cm^{-1}	$\Delta D/D$, %	Concn. (mol./l. $\times10^5$)	Classification
2S(Cu)	1000	16	1.204 (1.252)	
H(Cu)	1100	13	1.171 (1.257)	First group
Ch(Cu)	900	15	1.183 (1.251)	
NW(Cu)	0	3	1.195 (1.255)	
γ(Cu)	0	0	1.194 (1.256)	Second group
J(Cu)	0	3	1.194 (1.251)	

See the footnotes of Table II.

each observed with the same concentration as in the mixture. The order of magnitude of the difference between the sum (broken line) and the mixture (solid line) curves in Fig. 3 appears to be comparable with that of the equilibrium constants. Indeed, in the present case, comparing the differences of the two curves in the following values, i. e., the difference in wave number, $\Delta\nu$ cm^{-1}, of the two peaks (around 400 mμ) corresponding to the first band of G, and the decreasing ratio in optical density, $\Delta D/D$ %, at the maximum point (around 600 mμ) of the partner dye of G, it is seen that both of the orders of the values thus obtained are approximately parallel to that of K as shown in Table II. These values, therefore, may be taken as a measure for comparing the relative order of the amounts of complex formed.

Figure 4 shows the absorption spectra of mixtures of copper derivatives and the G dye observed in the same way as above. It is noticed in Fig. 4 that the copper dyes are divided into two classes; one is the class in which the dyes reveal apparent spectral differences, the other, the class in which the differences are extremely small. The values of $\Delta\nu$ and $\Delta D/D$ for these dyes are given in Table III, divided into two groups.

Discussion

When the dyes not containing copper are combined with the G dye, judging from the examples shown in Figs. 1 and 2, two sorts of complex 1 : 1 and 1 : 2 are formed. Moreover, the correlation between the first isosbestic point and the mixing ratio of the components indicates that in the region where the G concentration does not exceed that of the partner dye, only a 1 : 1 complex is formed. Accordingly, at the present stage, when only the 1 : 1 complex formation is to be considered, discussion will be possible under the conditions of relative concentration just mentioned. (A detailed investigation, including the 1 : 2 complex formation, will be undertaken in the next paper.) According to Table II, the order of the magnitudes of the equilibrium constant K for the formation of a 1 : 1 complex is approximately parallel to the order of $\Delta\nu$ and $\Delta D/D$ observed with the equimolar mixture. Therefore, at least insofar as the 1 : 1 complex formation is concerned, $\Delta\nu$ and/or $\Delta D/D$ may rather safely be employed instead of K as a relative measure of the extent of the formation of a 1 : 1 complex. Such a comparison by $\Delta\nu$ and $\Delta D/D$ will be made below.

The skeletal structure of dyes used here is sterically restricted by the introduction of copper[1]. Thus, first, the case of the copper derivatives (Table III) in which the steric condition is simplified will be discussed ; next, the case of those not containing copper (Table II) will be considered.

According to Table III, the magnitude of $\Delta D/D$ is about 15% for 2S(Cu), H(Cu) and Ch(Cu), but it is zero or almost zero for the rest, NW(Cu), γ(Cu) and J(Cu). These dyes can thus be clearly divided into two groups. A similar separation is even more distinctly revealed concerning the magnitude of the $\Delta\nu$ value ; the value for the former group is about 1000 cm^{-1} and for the latter, zero. So the dyes 2S(Cu), H(Cu) and Ch(Cu), which are considered to form a 1 : 1 complex to some extent, will be termed the first group, and the rest, considered to form no complex, the second group.

Since the G dye is the common ingredient of all the combinations used here, it must be considered that the results mentioned above were brought about by certain differences in the nature of the partner dyes. Now, as these dyes are copper derivatives, they are regarded as of sterically similar skeletal structure, as has already been established[1]. Consequently, as dominant factors responsible for the interaction with the G molecule, only two factors may be considered at the present stage, the number and the position of sulfonic groups, and the presence and the position of effective auxochromes (amino, hydroxyl). Discussion of these factors will be undertaken below.

First, let us consider the effect of the sulfonic groups. The nearer the sulfonic groups are to the center of the partner molecule, and the more the number of the groups, the smaller in amount should be the complex produced, because the repulsion of the ionic charges of the sulfonic groups from those in the G molecule probably acts to prevent the complex from being formed[*5]. According to Table III, however, the difference in position of the sulfonic groups of 2S(Cu) and H(Cu) of the first group is not appreciably revealed in the results. From a comparison of the results of the first and the second categories, it is also clear that those in the first category with more sulfonic groups produce more complexes, while those in the second category produce almost none. For the above reason, it may be said in this case that the ionic charge of the sulfonic group has no great influence in outline on the complex formation.

The other possible factor is the influence of the auxochromes. As has been pointed out before[4], the effect of the auxochromes upon the complex formation with the G dye is such that the complex is stabilized by the occurrence of an intermolecular charge-transfer through the auxochromes, and at the same time the $\Delta\nu$ value grows large. This is reflected in the fact that all the dyes in the first group with large $\Delta\nu$ values have amino or hydroxyl groups which are terminal groups of a conjugated system. On the other hand, in the second group, with zero values of $\Delta\nu$, NW(Cu) especially has no auxochromes of such kinds, and γ(Cu), though it has two amino groups, can also be considerd to have no effective auxochromes because they are not conjugated terminal groups in a usual sense. Thus, the expected effect of the auxochromes and the experimental results show a good correspondence. However, the case of the J(Cu) dye, which has amino groups as its conjugated terminal groups, deviates from the above reasoning ; the experimental results indicate that almost no complex is produced. However, whether or not amino groups of J(Cu) exerts a positive effect on the complex formation is obviously connected with its configuration relative to the G dye under the complex formation. Therefore, it is supposed here that the amino groups of J(Cu) could not reveal such a characteristic of auxochromes as seen in the

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[*5] The model of the complex formed assumes that the molecules overlap each other so as to be parallel longitudinally. See Ref. 4.

first group, owing to some reason, a correlation of geometric configuration, for instance.

Therefore, it may safely be said for the copper derivatives that the presence of the auxochromes as the terminal groups of a conjugated system is the necessary condition, even though not sufficient, to cause a spectral change with the formation of a complex.

Next, let us consider the case of Table II, where no copper is included. In this case, the hydroxyl group becomes free from copper to act as an effective auxochrome, and at the same time some dyes take a more planar structure as a result of being disengaged from the sterical restriction by copper. Namely, the 2S dye and the NW dye become more suitable structures for the complex formation than 2S(Cu) and NW(Cu) respectively, while the rest are left in nearly the same steric structure as the copper derivatives[1]. As mentioned above, the adding of effective auxochromes promotes the forming of a complex. Comparing Table II with Table III, the $\Delta\nu$ and $\Delta D/D$ of H, Ch, γ and J are evidently larger than those of the respective copper derivatives. This indicates the effect of hydroxyl. Moreover, according to the above considerations, 2S and NW ought to exhibit planar effects on their skeletal structures in addition to the effect of hydroxyl. Indeed, these dyes, as compared with 2S(Cu) and NW(Cu), respectively, show a more remarkable increase in $\Delta\nu$ and $\Delta D/D$ than expected from the hydroxyl effect. This indicates that the planar effect promotes the formation of a complex and, moreover, that it is quite large.

According to the qualitative results discussed above from Tables II and III, the disazo dyes must have effective amino or hydroxyl groups as auxochromes and be planar to some extent, in order to produce a complex by combination with G and to show the spectral change with the complex formation. Further, the sulfonic groups attached to the coupling components are important not because of the number of their ionic charges, but rather because of such steric effects as that the sulfonic groups prevent the dye from taking a more planar structure, or in some influence of their configuration relative to those of the G dye.

Thus, at the present time, nothing has been obtained more than a qualitative decision on the respective effects. However, some quantitative estimation of the effects will become possible after the detailed investigation being carried out on the equilibrium constants and their temperature dependence, etc., including the 1 : 2 complex formation.

Summary

1. The absorption spectra of the dyes prepared by coupling disazotized 2S-, H-, chromotropic, NW-, γ- and J- acid with dianisidine, and of their copper derivatives were observed in aqueous solutions of the binary mixture with Chrysophenine G, and were compared with the sum curves of the component absorption spectra.

2. The order of the equilibrium constants for a 1 : 1 complex formed between the dyes not containing copper and Chrysophenine G was parallel to the respective values of the difference in wave number ($\Delta\nu$ cm^{-1}) between maximum positions in the region of 390∼420 mμ of the curve simply added and that observed with the equimolar binary mixture of about 1×10^{-5}mol./l.; it was also parallel to those of the decreasing ratio in optical density ($\Delta D/D$) of the mixed system at the first maximum position of the sum curve.

3. Under the same conditions as above, $\Delta\nu$ and $\Delta D/D$ were also determined for the mixture of the copper derivatives and Chrysophenine G. In this case, the copper derivatives of 2S-, H-, and chromotropic acid, in the presence of effective auxochromes, still revealed large values of $\Delta\nu$ (ca. 1000 cm^{-1}) and $\Delta D/D$ (ca. 15%), while the values for the rest of the derivatives were almost zero.

4. Discussing the above results, it was shown that in order to display a spectral change due to the formation of a 1 : 1 complex in a binary mixture with Chrysophenine G, it is necessary that the partner dye has effective auxochromes (amino, hydroxyl) as terminal groups of a conjugated system. It was also shown that the sulfonic groups which are attached to the terminal naphthalene nuclei act on the structure of the dye itself as a steric factor rather than as an electric effect (repulsion) between the ionic charges in the groups and those of Chrysophenine G, and that the more planar structure, resulting in a smaller steric effect, produces more complex.

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