Absorptinon Spectra of Dyes. VIII.[1] The Correlation between Thermodynamic Quantities and Chemical Structure in Complex Formation*

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Previously,[1] the present authors have discussed the ease of the formation of complexes between Chrysophenine G and Chlorazol Sky Blue FF and similar skeletal dyes, from the viewpoints of the magnitudes of the equilibrium constant and of the spectral change. According to the conclusion reached, the partner dyes (to be abbreviated to P) of G (Chrysophenine G) have a negative effect on the complex formation when the P dyes have sulfonic groups at the positions adjacent to azo groups on the naphthalene rings. Further, the larger the number of effective auxochromes of P, the easier the formation of the complex, and the OH groups make the complex formation easier than NH_2 does. The above problem may be worth considering from the view-points of the strength of the connection between the component molecules forming a complex, and of the degree of the steric deformation and the restriction inflicted upon the molecule before and after the formation of a complex. Therefore, with the purpose of discussing again the above conclusion on a more rigid foundation, the authors measured a similar sample series at various temperatures. According to the free energy change, enthalpy change and entropy change thus obtained, the above-mentioned problem will be discussed for a 1 : 1 and a 1 : 2 complex formed between P and G.

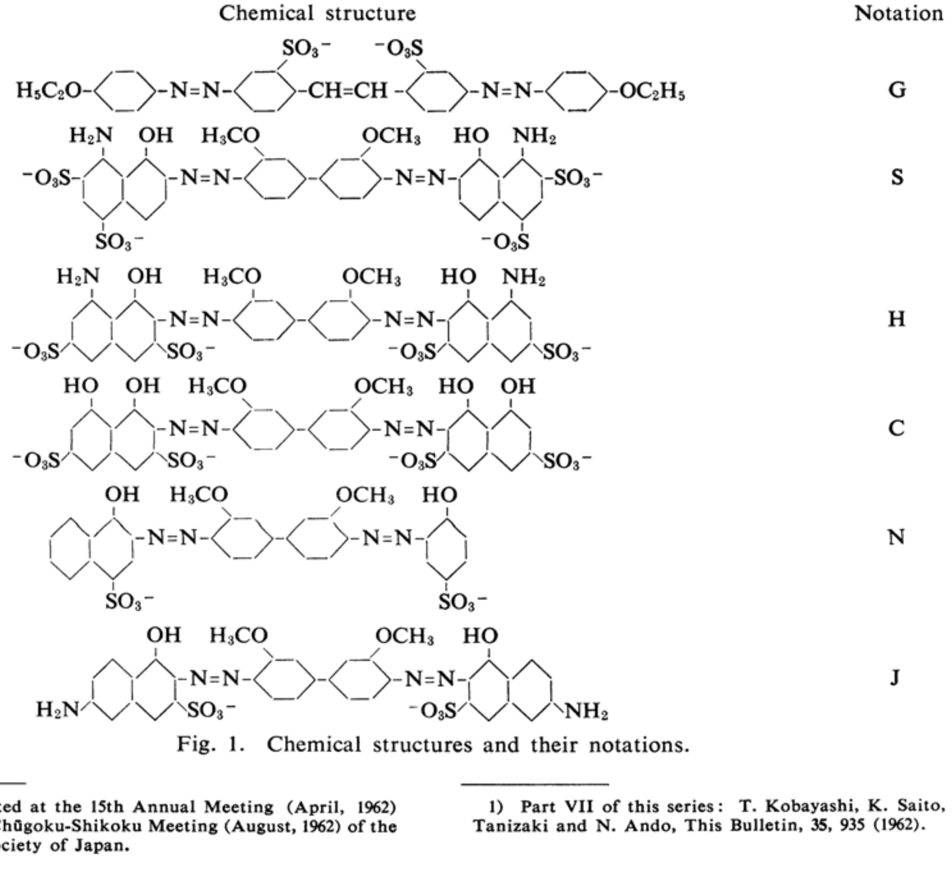

Fig. 1. Chemical structures and their notations.

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* Presented at the 15th Annual Meeting (April, 1962) and at the Chūgoku-Shikoku Meeting (August, 1962) of the Chemical Society of Japan.

[1] Part VII of this series: T. Kobayashi, K. Saito, Y. Tanizaki and N. Ando, This Bulletin, 35, 935 (1962).

Experimental

The chemical structures of the dyes used are shown in Fig. 1, along with the notations to be used here. Excepting G (Chrysophenine G), the notations are taken from the names of the coupling components. These are the same as the purified dyes used in the previous investigations.[1,2]

Water was used as the solvent. The dye solutions were prepared by using a mother solution of about 10^{-4} mol./l. All of the concentrations were determined by weight.

The absorption spectra were measured with a Shimadzu QR-50 spectrophotometer, the cell chamber of which was replaced by a larger one which contains cylindrical cells. The temperature of the cells was regulated by a specially-designed apparatus, and so could be kept within ±0.2°C of the desired temperature. The optical path of the cell is 20 mm. long, but it can be used, if necessary, as a 10 mm. path cell by the insertion of spacers. At each 10°C interval in the 20—60°C temperature range, the absorption spectra of the sample solutions were measured after they had been kept intact more than overnight after having been prepared. It has been confirmed that the temperature of the solution reaches the adjusted point within twenty minutes. All the measurements, therefore, were standardized so as to be started about twenty

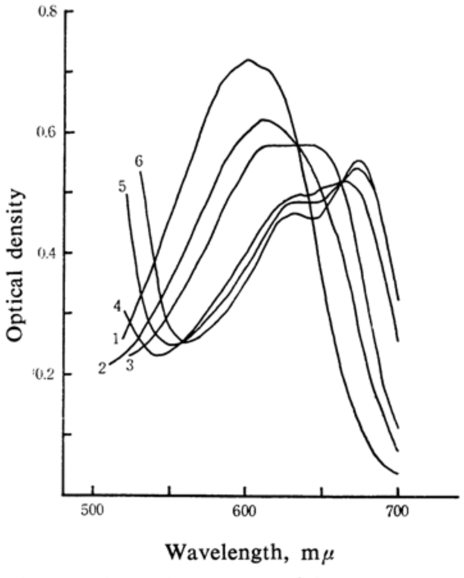

Fig. 2. Absorption spectra of C-G aqueous solutions: temp., 20°C; cell, 1 cm.

	G, mol./l.	C, mol./l.
1	0	9.293×10^{-6}
2	4.375×10^{-6}	9.293×10^{-6}
3	9.007×10^{-6}	9.293×10^{-6}
4	71.81×10^{-6}	9.293×10^{-6}
5	180.6×10^{-6}	9.293×10^{-6}
6	718.7×10^{-6}	9.293×10^{-6}

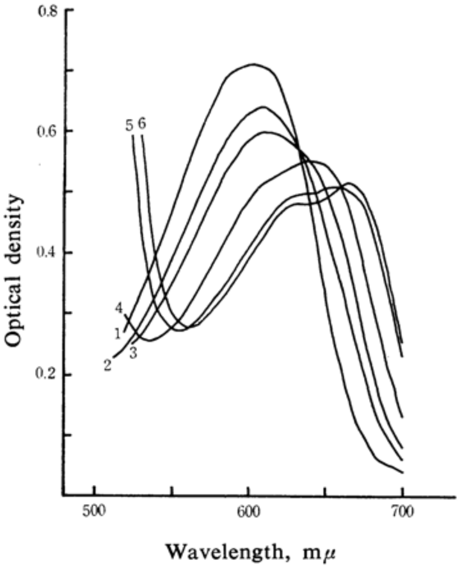

Fig. 3. Absorption spectra of G-C aqueous solutions: temp., 40°C; cell, 1 cm.

	G, mol./l.	C, mol./l.
1	0	9.293×10^{-6}
2	4.375×10^{-6}	9.293×10^{-6}
3	9.007×10^{-6}	9.293×10^{-6}
4	71.81×10^{-6}	9.293×10^{-6}
5	360.6×10^{-6}	9.293×10^{-6}
6	718.8×10^{-6}	9.293×10^{-6}

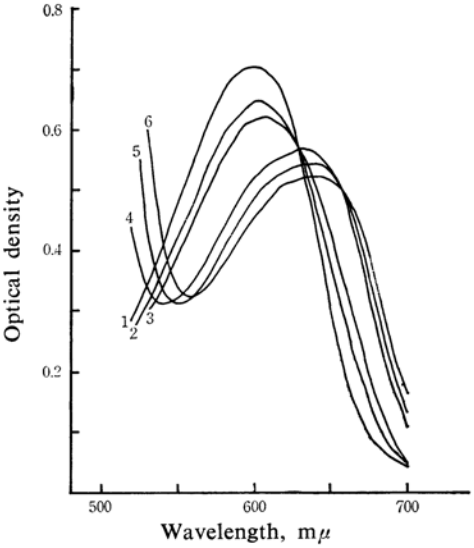

Fig. 4. Absorption spectra of G-C aqueous solutions: temp., 60°C; cell, 1 cm.

	G, mol./l.	C, mol./l.
1	0	9.293×10^{-6}
2	9.007×10^{-6}	9.293×10^{-6}
3	17.72×10^{-6}	9.293×10^{-6}
4	180.6×10^{-6}	9.293×10^{-6}
5	360.7×10^{-6}	9.293×10^{-6}
6	718.8×10^{-6}	9.293×10^{-6}

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2) T. Kobayashi, Y. Tanizaki and N. Ando, This Bulletin, 33, 913 (1960).

minutes after the solution had been kept at a constant temperature.

Results

Figures 2, 3 and 4 indicate the spectral change of the binary mixture of C and G when the concentration of C is varied, at 20, 40 and 60°C respectively. In every case well-defined isosbestic points exist at about 630 mμ and 660 mμ. The same tendency for the spectra to change was also found for the S-G system, and the appearance was the same as in the result already reported (ca. 27°C).[2] As has already been shown,[1] the first isosbestic points (ca. 630 mμ) of Figs. 2—4 indicate the co-existence of G and CG (1 : 1 complex), and the second, that of G and CG_2 (1 : 2). A quite similar tendency was observed for the binary mixture of G with any other dyes used. It is a matter of course, however, that the shapes of the individual bands and positions of the isosbestic points, etc., differed from one another according to the kinds of partner dyes.

TABLE I. EQUILIBRIUM CONSTANTS FOR THE 1 : 1 COMPLEX FORMATIONS AT VARIOUS TEMPERATURES

	$K_1\times 10^{-5}$, mol^{-1}l.				
P	20°C	30°C	40°C	50°C	60°C
S	600	210	61	14	5.3
H	35	7.0	1.8	0.58	0.18
C	—	50	7.0	2.4	0.77
N	5.3	4.4	2.3	1.7	1.1
J	—	1.4	0.73	0.32	0.22

TABLE II. EQUILIBRIUM CONSTANTS FOR THE 1 : 2 COMPLEX FORMATIONS AT VARIOUS TEMPERATURES

	$K_2\times 10^{-5}$, mol^{-1}l.				
P	20°C	30°C	40°C	50°C	60°C
S	2.8	1.0	0.29	0.12	—
H	0.048	0.022	0.0067	0.0025	—
C	0.31	0.12	—	—	—
N	0.80	0.65	0.36	—	—
J	—	0.031	0.020	0.0086	0.0070

TABLE III. FREE ENERGY-, ENTHALPY- AND ENTROPY- CHANGES FOR THE 1 : 1 COMPLEX FORMATIONS

	$-\Delta F_1$, kcal./mol.					$-\Delta H_1$ kcal./mol.	$-\Delta S_1$ e. u.
P	20°C	30°C	40°C	50°C	60°C		
S	10.4	10.1	9.7	9.1	8.7	24	44
H	8.8	8.1	7.5	7.0	6.5	25	57
C	—	9.3	8.4	7.9	7.4	27	60
N	7.7	7.7	7.7	7.7	7.7	7.4	−1
J	—	7.1	7.0	6.7	6.6	13	19

TABLE IV. FREE ENERGY-, ENTHALPY- AND ENTROPY-CHANGES FOR THE 1 : 2 COMPLEX FORMATIONS

	$-\Delta F_2$, kcal./mol.					$-\Delta H_2$ kcal./mol.	$-\Delta S_2$ e. u.
P	20°C	30°C	40°C	50°C	60°C		
S	7.3	6.9	6.4	6.0	—	20	45
H	4.9	4.6	4.1	3.6	—	19	47
C	6.0	5.7	—	—	—	19	40
N	6.6	6.7	6.5	—	—	6.7	0
J	—	4.9	4.7	4.3	4.3	11	20

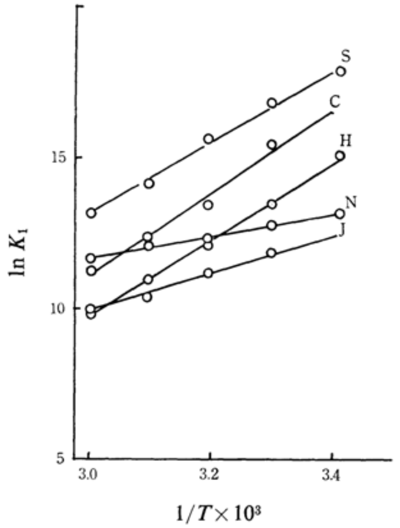

Fig. 5. Plots of ln K_1 vs. $1/T$ for the 1 : 1 P-G molecular complex formations.

Let P stand for the partner dye of G. If the following equilibriums exist for the 1 : 1 and 1 : 2 complex formation between P and G;

$$P + G = PG \qquad (K_1) \qquad (1)$$

$$PG + G = PG_2 \qquad (K_2) \qquad (2)$$

and if the mass action law can be applied, the respective equilibrium constants are expressed as follows;

$$K_1 = [PG]/[P][G] \qquad (3)$$

$$K_2 = [PG_2]/[PG][G] \qquad (4)$$

where [P], [G], etc. represent the respective equilibrium concentrations. K_1 and K_2 were calculated following the method described in the Appendix. The data are shown in Tables I and II respectively. In the usual way, the free energy change ($-\Delta F$) was obtained from the values of K_1 and K_2 shown in Tables I and II. The results obtained are given in Tables III and IV respectively. The relation between ln K and $1/T$ (T: absolute temperature) was plotted in Figs. 5 and 6. By the application of the method of least squares, regarding the relation as linear, we obtained the enthalpy change ($-\Delta H$) and the entropy change ($-\Delta S$) from, respectively, the values of the slope and the intercept of the straight line and the ln K axis. The results for a 1 : 1 and a 1 : 2 complex are shown in the corresponding columns of Tables III and IV respectively.

Discussion

The Free Energy Change.—A criterion of the facility of the complex formation in the system under consideration has already been made by means of the magnitude of the equilibrium constant[1] in the relationship $-\Delta F=\boldsymbol{RT}\ln K$. As the free energy change is combined with the equilibrium constant, $-\Delta F$ as well as K can be adopted as a measure of the criterion of the complex formation. In this paper, the discussion will be made in terms of $-\Delta F$.

The plotting of the $-\Delta F$ values against the temperature in Tables III and IV gives the relations shown in Figs. 7 and 8 respectively. In each case the relation is regarded as linear. According to Fig. 7 the inclinations of lines of S, C and H are large in about the same order, while those of N and J are nearly horizontal. By comparing the chemical structures of these two classes shown in Fig. 1, it may be seen that S, C and H each has four sulfonic groups and two effective auxochromes, while the class of N and J has only two sulfonic groups and two effective terminal auxochromes.[1] It seems that there is some correlation between this fact and the behavior of the $-\Delta F$ value against the temperature.

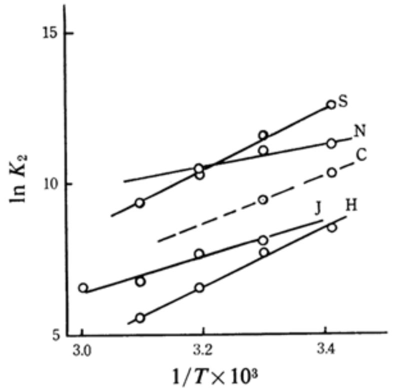

Fig. 6. Plots of ln K_2 vs. $1/T$ for the 1 : 2 P-G molecular complex formations.

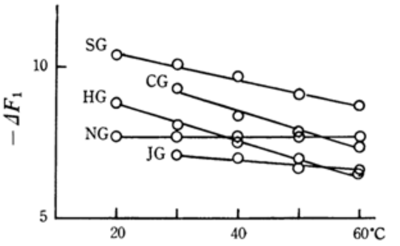

Fig. 7. Relation of $-\Delta F$ vs. temperature.

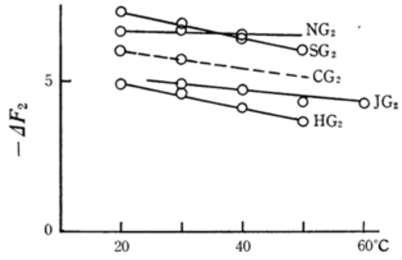

Fig. 8. Relation of $-\Delta F$ vs. temperature.

There are also the following differences among the dyes of the respective classes. The magnitudes of the $-\Delta F$ values at any temperature are in the order of S, C and H (Fig. 7), and the difference in the chemical structures may be seen in the location of the sulfonic group and the sort of auxochrome. The facility of the 1 : 1 complex formation had already been discussed in terms of the difference in chemical structure.[1] Moreover, the conclusion derived from the discussion comes into existence over the temperature range observed here. Again, the relation between the difference of the $-\Delta F$ values of N and J and the positions of the sulfonic groups may be interpreted in terms of conclusion mentioned above.

It is clear from an inspection of Fig. 8 that there is also approximately the same relationship as above in the case of the 1 : 2 complex formation.

The so-called standard affinity $(-\Delta\mu^\circ)$ has been used extensively as a measure of the substantivity of dyes. However, $-\Delta\mu^\circ$ and $-\Delta F$ are identical in physical meaning. The expression of $-\Delta\mu^\circ$ involves a quantity which represents a surface volume in the substrate.[3] This can be regarded as a parameter for matching the dimensions of the dye concentrations in both phases of the solution and in the substrate of cellulose. However, it is not always easy to estimate the surface volume. In any case, Table V illustrates the affinity values of S (Chlorazol Sky Blue FF) and G (Chrysophenine G) quoted from those obtained for various cellulose-substrates. If the relation of $-\Delta\mu^\circ$ and temperature is plotted using the

TABLE V. STANDARD AFFINITIES ($-\Delta\mu^\circ$, cal./mol.) AND HEATS OF DYEING ($-\Delta H^\circ$, kcal./mol.)

D	60°C	70°C	80°C	90°C	100°C	$-\Delta H^\circ$
S	7500	6600	6300	6100	5900	22
G	3800	3400	3200	3000	2600	14

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[3] T. Vickerstaff, "The Physical Chemistry of Dyeing," 2nd Ed., Oliver and Boyd, London (1954), p. 195.

values in Table V, a tendency similar to that of Fig. 7 will be obtained. The heat of the dyeing ($-\Delta H°$) of S and G are, respectively, 22 and 14 kcal. (Table V). The values for many other direct dyes are also in the same order and correspond to the magnitude of $-\Delta H$ in Tables III and IV. Accordingly, the relative order of substantivity can be compared by the use of $-\Delta F$ values for the complex formation or by the use of $-\Delta H$ values, without using the standard affinity involving various problems.

The Enthalpy Change.—The magnitudes of the enthalpy change for the class of S, C, and H, and the class of N and J, classified in the foregoing section apparently differ from each other, as may be seen from Tables III and IV. According to the comparison of the mean values for the respective classes, the $-\Delta H_1$ and $-\Delta H_2$ values for the former class are 2—2.5 times as large as those for the latter. As is well known, the dyeing mechanism of direct dyes believed in at the present time involves mainly the formations of the hydrogen bond and the dispersion force. The magnitude of the dispersion force is considered to be dependent upon the extension of the electron cloud on the faced molecules, namely, in this case the dimensions of the confronted molecular surface. However, such a difference may not be so large with regard to the partner dyes used here. In the meanwhile, the formation of the intermolecular hydrogen bond in the complex under consideration is impossible in the usual way. However, if the auxochromes contribute to the complex formation in some way other than hydrogen bonding, the fact that the class of S, C and H has twice as many auxochromes as the class of N and J corresponds well with the fact that the former class produces an 2—2.5 times as much energy of formation as the latter. In this case, therefore, it is considered that the lone paired electrons on the functional group (auxochrome) play an important role in forming the complex.

The only difference in the chemical structures of C and H is that the OH groups are the auxochromes for the former, while the NH_2 groups are for the latter in the same positions. For that reason, the bonding energies should be compared with respect to the distinction of the auxochromes. Unfortunately, however, no conclusion could be obtained for the subject just mentioned because of the small number of proper samples used in the the present experiment.

The Entropy Change.—By the use of the entropy change, the degree of the restriction of the partner dye in the complex formation will be compared, and also the deformation of the sterical structure will be discussed. It is a matter of course that the G molecule undergoes a similar change through a complex formation, but the degree of change should be correlated with that of the partner dye. Because G is the common ingredient, it is possible to regard the apparent entropy change as a relative measure of the entropy change of the partner dye itself. The magnitudes of the $-\Delta S$ values in Tables III and IV are divided again into the class of S, C, and H and the class of N and J. The magnitudes of the former class are much larger than those of the latter. This fact may be interpreted as due to the following reason. As has been described above, all of the former, which have twice as many functional groups as the latter, can form a more compact complex, so the component in a complex undergoes the stronger restriction. The freedom is decreased, therefore, and $-\Delta S$ is necessarily increased. Among the classes of S, C and H, S and H differ from each other only in the attached positions of the sulfonic groups, while C and H differ only in the kinds of functional groups (Fig. 1). As for the $-\Delta S_1$ value for a 1:1 complex, in Table III the value for S is about 44 e.u. while those of C and H are, respectively, about 57 e.u. and 60 e.u. which are regarded as nearly equal and are considerably larger than that of S. This great difference must be due to the location of the sulfonic groups. The same situation is found in N and J. In the case of a 1:2 complex (Table IV), the same relationship can be seen if the result of C which was based on only two experimental values ($-\Delta F_2$) is excluded because of its weak support.

The sulfonic groups of J and those in the inner position of C and H (see Fig. 1) make the plane of the naphthalene nuclei deviate largely from the molecular plane.[2] Accordingly, if it is assumed that all the partner dyes take a similar sterical configuration in the complex state, the above-mentioned difference in $-\Delta S_1$ suggests that partner molecule is more planar in the 1:1 complex state than in the free state. This is because a larger deformation is required for C and H than for S to be brought to the similar planar structure. The same thing can be said for the case of N and J.

It may be noticed in Tables III and IV that the $-\Delta S$ values for N are nearly zero through the formation of a 1:1 and 1:2 complex. In the foregoing discussion solvation has not been taken into account. The effect of solvation should be included naturally in the $-\Delta S$ (and $-\Delta H$) values obtained here. Therefore, the fact that the absolute entropy in the N-G system is not changed by the complex formation might suggest that, in the course of the complex formation, the solvent molecules which lie between G and N are removed, and that the intermolecular force between G and N formed instead of the hydration restricts the system to the same degree as the hydrated state.

Summary

1) Using five kinds of dyes of Sky Blue FF and of similar structures, the equilibrium constants for a 1 : 1 and a 1 : 2 complex formed with Chrysophenine G have been determined by means of spectroscopy in the intervals of 20—60°C.

2) A new method of calculating the equilibrium constant has been proposed.

3) The free energy change ($-\Delta F$), the enthalpy change ($-\Delta H$) and the entropy change ($-\Delta S$) for the complex formation have been obtained.

4) The correlation between these quantities and the chemical structure has been discussed and the following facts clarified: The larger the number of effective auxochromes (NH_2, OH), the greater $-\Delta H$ and $-\Delta S$ become. The sulfonic group contributes to $-\Delta S$ through the location of that group. The dye molecule in the complex state is more planar than in the free state.

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Appendix

As the method of determining the equilibrium constant by utilizing the change in spectra, the Benesi-Hildebrand method[4] has been applied most extensively. Various other methods are also known. In the case of the present investigation, however, the equilibrium constants can be evaluated easily and precisely by utilizing the two isosbestic points, and by following the treatment described below.

When P, G, PG and PG_2 species are in equilibrium and the respective absorption coefficients are ε_P, ε_G, etc. at any wavelength, the optical density, D, of the system is expressed as follows:

$$D=[P]\varepsilon_P+[G]\varepsilon_G+[PG]\varepsilon_{PG}+[PG_2]\varepsilon_{PG_2} \tag{5}$$

Two isosbestic points appear for the system under consideration. In the wavelength region at which the component G does not absorb light, ε_G is zero. In this region, and yet in the concentration range in which the first isosbestic point is kept, $[PG_2]=0$; hence, Eq. 5 is simplified to Eq. 6:

$$D=[P]\varepsilon_P+[PG]\varepsilon_{PG} \tag{6}$$

Expressing the initial concentration by P_0, the optical density (D_0) before G is added is:

$$D_0=P_0\varepsilon_P \tag{7}$$

Hence, we obtain from Eqs. 6 and 7:

$$\Delta D=D_0-D=(P_0-[P])\varepsilon_P-[PG]\varepsilon_{PG}$$
$$=[PG](\varepsilon_P-\varepsilon_{PG})$$

or

$$\Delta D=\varepsilon_1[PG] \tag{8}$$

were $\varepsilon_P-\varepsilon_{PG}=\varepsilon_1$. From Eqs. 3 and 8, therefore, the equilibrium constant, K_1, becomes:

$$K_1=\Delta D/\varepsilon_1(P_0-\Delta D/\varepsilon_1)(G_0-\Delta D/\varepsilon_1) \tag{3$'$}$$

where P_0 and G_0 stand for the respective initial concentrations of P and G.

Next, in the concentration range in which the second isosbestic point is kept, $[P]=0$ because all of the species must be completely changed to the complexes. Therefore, Eq. 5 becomes:

$$D=[PG]\varepsilon_{PG}+[PG_2]\varepsilon_{PG_2} \tag{6$'$}$$

By putting D_0' as the optical density for the initial concentration of the PG component corresponding to Eq. 2, and by taking into account the fact that the difference between that initial concentration and [PG] is $[PG_2]$, we obtain the following equation, corresponding to Eq. 8:

$$\Delta D'=D_0'-D=[PG_2](\varepsilon_{PG}-\varepsilon_{PG_2})$$

or

$$\Delta D'=\varepsilon_2[PG_2] \tag{8$'$}$$

where $\varepsilon_2=\varepsilon_{PG}-\varepsilon_{PG_2}$. The equilibrium constant, K_2, for Eq. 4 may then be expressed as follows:

$$K_2=\Delta D'/\varepsilon_2(P_0-\Delta D'/\varepsilon_2)(G_0-P_0-\Delta D'/\varepsilon_2) \tag{4$'$}$$

Now, when K_1 and K_2 are evaluated according to Eqs. 3$'$ and 4$'$, the question arises of how ε_1 and ε_2 are determined. This problem can be solved simply by utilizing the isosbestic points as described below. At first, the second isosbestic point (a letter II will be affixed to indicate the position of that wavelength) is noticed in order to determine ε_1. Thus, Eq. 6$'$ holds for the optical density, and besides $\varepsilon^{II}_{PG}=\varepsilon^{II}_{PG_2}$; therefore,

$$D^{II}=([PG]+[PG_2])\varepsilon^{II}_{PG} \tag{9}$$

Taking into account that $([PG]+[PG_2])=P_0$ is true in the concentration range where the second isosbestic point is kept, Eq. 9 may be rewritten as Eq. 10;

$$\varepsilon^{II}_{PG}=D^{II}/P_0 \tag{10}$$

On the other hand, as ε^{II}_P is obtained directly by Eq. 7, $\varepsilon^{II}_P-\varepsilon^{II}_{PG}=\varepsilon^{II}_1$ is determined. Consequently, by substituting ε^{II}_1 and the density-difference ΔD^{II} at the wavelength of the second isosbestic point, respectively, into ε_1 and ΔD of Eq. 3$'$, K_1 may be evaluated. Similarly, K_2 can be calculated by utilizing the first isosbestic point. That is to say, in this case, Eq. 6 holds, $\varepsilon^I_P=\varepsilon^I_{PG}$, and $([P]+[PG])=P_0$, so that the relation $\varepsilon^I_{PG}=D^I/P_0$ is derived. On the other hand, with the condition $P_0\ll G_0$, $\varepsilon^I_{PG_2}$

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[4] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

can be determined as the quotient of the optical density, D^{I}, at the wavelength of the first isosbestic point divided by P_0. From Eq. 4′, K_2 can be calculated by using the $\varepsilon^{\mathrm{I}}_2$ $(=\varepsilon^{\mathrm{I}}_{\mathrm{PG}}-\varepsilon^{\mathrm{I}}_{\mathrm{PG2}})$ value thus obtained and the density-difference, ΔD^{I}, at the same wavelength.