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Studies of the Aggregation of Dyes. A Spectrophotometric Method of Determining the Aggregation Numbers of Dyes

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The aggregation of dyes in an aqueous or alcoholic solution has been studied spectroscopically by a method named the "maximum slope method." The method can ascertain the molar absorptivity and formation constant of dye aggregate when a simple equilibrium model between a monomer and an n-mer is assumed to be operative, and when the absorptivity of monomer is given. Further, the molar absorptivities of the monomer and the polymers and the formation constants of the polymers are adjusted, in order to minimize the mean deviation, by an other method, named the "minimum deviation method." Using the latter method, the parameters of an equilibrium system including a monomer and several polymers can also be calculated. Aggregations of Benzopurprine 4 B and Sky Blue FF in aqueous salt solutions were studied by the above two methods. Aggregations of these dyes in aqueous alcoholic solutions were also discussed.

In resent years, the solvent-assisted dyeing of wool goods by acid dyes has been developed for the industrial use, and several fundamental discussions of the mechanism of solvent dyeing have been reported.[1,2]

Yabe and Hayashi[3,4] have already reported on the extraordinarily quick and high absorption of direct dyes on cellulose in the H_2O/n-BuOH dyebath system, and compared the absorption spectrum of the cellophane dyeings from normal and solvent-assisted systems.

A new way of determining the aggregation numbers of organic substances including dyes in solution has to be developed, as the physical state of direct dyes in solution is supposed to influence greatly on that of dyes on the substrates. This report may contribute to clarify the aggregation of dye molecules in solution.

When a dye aggregates in solution, the molar absorptivity (ε) changes with an increase in the dye concentration; it shall be given by a weighted mean of the molar absorptivities of each aggregate (Eq. (1)):

$$\varepsilon = \sum_{i=1}^{n} f_i \varepsilon_i, \qquad (1)$$

where ε_i is the molar absorptivity of the pure i-mer, and f_i, the corresponding molar fraction. Since the equilibrium constant, K_i and ε_i can not be determined from Eq. (1) alone, a simple equilibrium between the monomer and a polymer of only one distinct degree of aggregation is assumed[*1]; then:

$$\varepsilon = f_1 \varepsilon_1 + f_n \varepsilon_n, \qquad (2)$$

$$1 = f_1 + n f_n. \qquad (3)$$

If the activity coefficients are assumed to be constant in the concentration range studied, we have:

$$f_n = K_n C_1^n C, \qquad (4)$$

where C_1 and C are the monomer and the total dye concentration respectively. By combining Eq. (2) with Eqs. (3) and (4), we get Eq. (5):

$$\log C(\varepsilon_1 - \varepsilon) = n \log C(\varepsilon - \bar{\varepsilon}_n) + \log n K_n (\varepsilon_1 - \bar{\varepsilon}_n)^{1-n}. \qquad (5)$$

In Eq. (5), ε_n/n is designated as $\bar{\varepsilon}_n$. Hence, if $\log C(\varepsilon_1 - \varepsilon)$ is plotted against $\log C(\varepsilon - \bar{\varepsilon}_n)$, the points should lie on a straight line, the slope of which gives the degree of aggregation (n), and the equilibrium constant (K_n) can

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[1] L. Peters and C. B. Stevens, *J. Soc. Dyers & Colourists*, **72**, 241 (1956).

[2] M. Korrholm and J. Lindberg, *Text. Res. J.*, **26**, 528 (1956).

[3] M. Hayashi, Y. Matsumoto and A. Yabe, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **67**, 221 (1964).

[4] M. Hayashi, K. Kawabata, Y. Matsumoto and A. Yabe, *ibid.*, **69**, 1176 (1966).

[*1] This simplifying assumption of the monomer-n-mer equilibrium model has been accepted as being consistent in many dye aggregation systems.

be calculated from the intercept. By assuming suitable values for ε_1 and $\bar{\varepsilon}_n$, Kuhn[5] has shown that the association degree of sodium phthalocyaninetetrasulfonate is 2 and 4 in, respectively, lower and higher concentration ranges in aqueous solutions, while Zanker[6] and Mataga[7] suggested neglecting the $\bar{\varepsilon}_n$'s of basic dyes in the calculation of Eq. (5), as they are too small compared with ε and ε_1. However, the values of ε_1 and $\bar{\varepsilon}_n$ are not always determined accurately, or $\bar{\varepsilon}_n$ cannot be neglected, especially when the polymer band does not differ very much from the monomer band. In such cases, therefore, it seems difficult to obtain reliable results by the use of Eq. (5).

In an attempt to avoid these difficulties, Hosoya and Nagakura computed the ε_1, ε_2 and K_2 of benzoic acid in the dimerisation stage in an aqueous solution by means of least-squares calculation.[8] The method developed by them affords the most reliable results, but the computations must be carried out on a computer, since the least-squares calculation had to be repeated until the parameters converge to certain values.

The present authors have, therefore, developed a method, named the "maximum slope method,"[*2] which involves a simpler computation and less supposition, and which still gives more reliable results.

Theoreticals

(1) **Maximum Slope Method.** Equation (6) is derived from Eq. (5):

$$\frac{1}{n-1}\log(\varepsilon_1-\varepsilon)-\frac{n}{n-1}\log(\varepsilon-\bar{\varepsilon}_n)=\log\alpha C,$$

$$\alpha=(nK_n)^{1/(n-1)}(\varepsilon_1-\bar{\varepsilon}_n). \qquad (6)$$

Taking $\log\alpha C=X$, Eq. (6) reads:

$$\frac{1}{n-1}\log(\varepsilon_1-\varepsilon)-\frac{n}{n-1}\log(\varepsilon-\bar{\varepsilon}_n)=X. \qquad (7)$$

The curve of ε *vs.* $\log C$ can be correlated with the curve of ε *vs.* X as follows.

(1) The two curves can be superposed on each other by sliding over the abscissa for some distance ($\log\alpha$); equilibrium constant (K_n) can thus be calculated.

(2) The maximum slope of the tangents of two curves ($\varepsilon-\log C$ and $\varepsilon-X$) are equal to each other; that is,

$$(\mathrm{d}\varepsilon/\mathrm{d}(\log C))_{\max}=(\mathrm{d}\varepsilon/\mathrm{d}X)_{\max}$$
$$=-2.3\left(\frac{\sqrt{n}-1}{\sqrt{n}+1}\right)(\varepsilon_1-\bar{\varepsilon}_n)$$

(3) The maximum slope is proportional to $(\varepsilon_1-\bar{\varepsilon}_n)$. The values of $\bar{\varepsilon}_n$, K_n and n are obtained by the following procedure on the basis of these three correlations:

(1) The maximum slope (m_0) of the tangent of the plotted curve ($\varepsilon-\log C$) is determined, and the absorptivity ε_1 is evaluated by extrapolating to an infinite dilution.

(2) On substituting a suitable value for $\bar{\varepsilon}_n$, and 2 for n, the X's corresponding to ε's are computed from Eq. (7).

(3) Then the maximum slope (m) of the tangent of the curve ($\varepsilon-X$) is determined. In general, m is not equal to m_0, because $\bar{\varepsilon}_n$ is not the true value. However, $\bar{\varepsilon}_n$ can easily be adjustable to its true value ($(\bar{\varepsilon}_n)_0$) by Eq. (9):

$$m_0/m=(\varepsilon_1-(\bar{\varepsilon}_n)_0)/(\varepsilon_1-\bar{\varepsilon}_n) \qquad (9)$$

(4) The curve ($\varepsilon-X$) is slided over the abscissa until the two tangential maximum-slope are superposed.

(5) These fitting processes are also carried out on $n=3$, 4, and so on.

(6) Then, we determine the theoretical n value which best fits the experimental curve.

Hosoya and Nagakura's results on the dimerisation of benzoic acid in an aqueous solution[8] have been analysed by this maximum slope method, and the final values of ε_1, ε_2 and K_2 and the accuracy were compared with those obtained by the repeated least-squares method by the above authors (Table

TABLE 1. DIMERISATION OF BENZOIC ACID

method	I[a]	II[b]	III[c]
$\varepsilon_1\times10^{-3}$	0.870	0.887	0.868
$\varepsilon_2\times10^{-3}$	3.300	3.274	3.240
$K\times10^{-3}$	0.659	0.661	0.795
Mean deviation (%)[d]	0.58	0.32	0.59

a) Maximum slope method

b) Minimum deviation method

c) Parameters given by Hosoya and Nagakura (Ref. 8)

d) Mean deviation $=N/100\sum|\varepsilon_{obs}-\varepsilon_{calc}|/\varepsilon_{obs}$, where ε_{obs} and ε_{calc} are apparent observed and calculated molar absorptivities, and N is number of data.

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[5] H. Kuhn, E. Schnabel and H. Nöther, "Recent Progress in the Chemistry of Natural and Synthetic Colour Matters and Related Field," ed. by T. S. Gore, Academic Press (1962), p. 561.

[6] V. Zanker, *Z. Phys. Chem.*, **200**, 250 (1952).

[7] N. Mataga, This Bulletin, **30**, 375 (1957).

[8] H. Hosoya and S. Nagakura, *J. Mol. Spectroscopy*, **8**, 257 (1962).

[*2] This method has been developed quite independently by the authors, but it has proved to be quite similar in idea to the one which had already been reported by Sanders and Hyne[9] for analyzing the NMR spectra of associated alcohols and phenol.

[9] M. Sanders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

1). Table 1 shows that the accuracy of the maximum slope method is as good as that of the repeated least-squares method.

(2) **The Minimum Deviation Method.** In spite of its usefulness, the maximum slope method has the defect that one should assume a definite value of ε_1, for an error involved in the evaluation of ε_1 may result in some uncertainty in the $\bar{\varepsilon}_n$, K_n or even n value estimated. In this respect, the values, ε_1, $\bar{\varepsilon}_n$ and K_n obtained from the maximum slope method must be readjusted to minimize the possible errors by the minimum deviation method. The mathematical procedure is as follows:

The zero approximations, $(\varepsilon_1)_0$, $(\bar{\varepsilon}_n)_0$ and $(K_n)_0$, are chosen as the values obtained by the maximum slope method. The calculated absorptivities, $\varepsilon_{\text{calc}}$, are obtained from Eq. (2′) using the monomer concentrations, C_1, obtained by solving Eq. (10):

$$\varepsilon_{\text{calc}} = (\varepsilon_1 C_1 + n\bar{\varepsilon}_n K_n C_1{}^n)/C \qquad (2')$$

$$C = C_1 + nK_n C_1{}^n \qquad (10)$$

A mean deviation ($\varDelta$) is given by Eq. (11):

$$\varDelta = \frac{1}{N}\sum|\varepsilon_{\text{calc}} - \varepsilon_{\text{obs}}|/\varepsilon_{\text{obs}}$$

The effects (δ) of changing each parameter by 0.1% on the mean deviation are determined to be:

$$\left.\begin{aligned} \delta_1 &= \varDelta(1.001\,\varepsilon_1, \bar{\varepsilon}_n, K_n) - \varDelta(\varepsilon_1, \bar{\varepsilon}_n, K_n) \\ \delta_2 &= \varDelta(\varepsilon_1, 1.001\,\bar{\varepsilon}_n, K_n) - \varDelta(\varepsilon_1, \bar{\varepsilon}_n, K_n) \\ \delta_3 &= \varDelta(\varepsilon_1, \bar{\varepsilon}_n, 1.001\,K_n) - \varDelta(\varepsilon_1, \bar{\varepsilon}_n, K_n) \end{aligned}\right\} \qquad (12)$$

Then, all the parameters are simultaneously changed in proportion to $\varepsilon_1\delta_1$, $\bar{\varepsilon}_n\delta_2$, and $K_n\delta_3$, respectively, until no further decrease in the mean deviation is found. Thus, the new parameters, the higher approximations, are obtained, and again their effects on the mean deviation are determined; the same fitting process continues until no further decrease in the mean deviation is possible.*3

The results refined by the minimum deviation method are compared with those obtained by the maximum slope method and those obtained by the least-squares method in Table 1. It can be seen that a combination of the maximum slope method with the minimum deviation method can give the best fit of the experimental curves of ε *vs.* $\log C$. Also, it is noticeable that the results obtained by the maximum slope method do not differ much from the best values.

When the mean deviations of several monomer-n-mer models are similar to one another, one should also consider models including all or some of those n-mers; that is,

$$mD \rightleftarrows D_{m_1} + D_{m_2} + \cdots + D_{m'} \qquad (13)$$
$$(m = \sum m_i)$$

In this case the monomer concentration is obtained by solving Eq. (14), instead of Eq. (10), and $\varepsilon_{\text{calc}}$ is computed by Eq. (15):

$$C = C_1 + m_1 K_{m_1} C_1{}^{m_1} + \cdots + m' K_{m'} C_1{}^{m'} \qquad (14)$$

$$\varepsilon_{\text{calc}} = (\varepsilon_1 C_1 + \varepsilon_{m_1} K_{m_1} C_1{}^{m_1} + \cdots + \varepsilon_{m'} K_{m'} C_1{}^{m'})/C \qquad (15)$$

The ε_i and K_i values of each polymer, as evaluated by the above-described procedure, were taken as the zero approximation and were treated by a process similar to the minimum deviation method.

Results and Discussions

(1) **Benzopurprine 4B (C.I. Direct Red 2) in an Aqueous Salt Solution.** Benzopurprine 4B did not aggregate in an aqueous solution; no change in absorptivity was observed in the concentration range between 10^{-7} and 10^{-4} mol/*l*.*4

On the other hand, upon the addition of

TABLE 2. THE AGGREGATION PARAMETERS OF BENZOPURPINE 4B AT SALT CONCENTRATION OF 20 mmol/*l*

Monomer-*n*-mer equilibrium model*

n	2	3	4
$\varepsilon_1 \times 10^{-5}$	0.5 (0.504)	0.5 (0.503)	0.5 (0.501)
$\varepsilon_n \times 10^{-5}$	0.838 (0.822)	1.275 (1.265)	1.720 (1.695)
$K_n \times 10^{-5(n-1)}$	1.62 (1.62)	5.92 (5.92)	18.76 (18.76)
Mean deviation (%)	1.44 (1.20)	1.37 (1.27)	1.61 (1.39)

Models including two or three polymers

Polymer included**	2+3	2+3+4
$\varepsilon_1 \times 10^{-5}$	0.511	0.510
$\varepsilon_2 \times 10^{-5}$	0.857	0.869
$\varepsilon_3 \times 10^{-5}$	1.260	1.318
$\varepsilon_4 \times 10^{-5}$	—	1.663
$K_2 \times 10^{-5}$	1.617	1.620
$K_3 \times 10^{-10}$	5.913	5.917
$K_4 \times 10^{-15}$	—	18.73
Mean deviation (%)	1.25	1.22

*The parameters computed by minimum deviation method are given in parenthesis.

**For example, 2+3 shows a model including dimer and trimer.

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*3 In actuality the process was stopped when $\varDelta$ increased with variations in ε_1, $\bar{\varepsilon}_n$, and K_n by $\varepsilon_1\delta_1$, $\bar{\varepsilon}_n\delta_2$, and $K_n\delta_3$ respectively.

*4 The constancy of molar absorptivity does not always preclude the existence of aggregates in solution. Much work has to be done in this connection.

salt (NaCl) the absorption spectrum shifted both hypso- and hypochromicaly; this shows the formation of dye aggregates in an aqueous salt solution. Table 2 shows the aggregation parameters at a salt concentration of 20 mmol/*l* and also the mean deviations of models, including monomer to tetramer; the latter appear to be similar to one another, although the deviation of the monomer-dimer system is the least. Unfortunately, we could not decide from the point of view of statistical analysis which model was preferable, because of the inevitable experimental errors.

The parameters at a salt concentration of 40 mmol/*l* are compared in Table 3. A statistical analysis showed that the monomer-dimer and monomer-dimer-trimer-tetramer models could be discarded, because of their large deviations. Thus, the monomer-dimer-trimer, monomer-trimer, and monomer-tetramer models are preferable in this case from the point of view of statistical analysis. On the other hand, Fig. 1 shows that the monomer-trimer model approximates the monomer-dimer-trimer model because of the negligible contribution of the dimer fraction in this case. If we assume that, in the aggregation stage of Benzopurprine 4B, several polymers exist together rather than a single polymer, and if the monomer-*n*-mer model can be considered as an approximation of the model including the monomer and all or some of the polymeres up to *n*-mer, the most preferable model among the models shown in Table 3 is the monomer-dimer-trimer model. Hence, the most preferable model at a salt concentration of 20 mmol/*l* may be determined to be among the monomer-dimer, monomer-trimer and monomer-dimer-trimer models. Figure 2 shows that the contribution of the dimer at a salt concentration of 20 mmol/*l* is larger than that at 40 mmol/*l*.

TABLE 3. THE AGGREGATION PARAMETERS OF BENZOPURPRINE 4B AT SALT CONCENTRATION OF 40 mmol/*l*

Models including single polymer

n	2	3	4
$\varepsilon_1 \times 10^{-5}$	0.5 (0.506)	0.5 (0.504)	0.5 (0.509)
$\varepsilon_n \times 10^{-5}$	0.712 (0.718)	1.242 (1.235)	1.760 (1.697)
$K_n \times 10^{-5(n-1)}$	0.601 (0.599)	6.21 (6.21)	102.9 (102.9)
Mean deviation (%)	1.55 (1.09)	0.53 (0.46)	2.35 (0.55)

Models including several polymers

Model	2+3	2+3+4
$\varepsilon_1 \times 10^{-5}$	0.509	0.515
$\varepsilon_2 \times 10^{-5}$	0.715	0.714
$\varepsilon_3 \times 10^{-5}$	1.267	1.244
$\varepsilon_4 \times 10^{-5}$	—	1.718
$K_2 \times 10^{-5}$	0.600	0.600
$K_3 \times 10^{-10}$	6.21	6.21
$K_4 \times 10^{-15}$	—	102.8
Mean deviation (%)	0.49	0.74

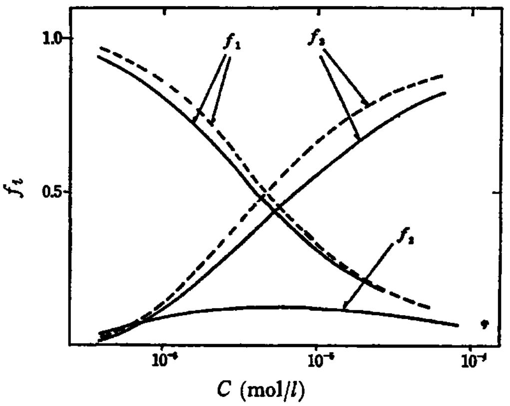

Fig. 1. Mole fractions of polymers *vs*. dye (Benzopuprine 4B) concentration (salt concentration; 40 mmol/*l*). ($f_i = iC_i/C$)
—— monomer-dimer-trimer model
- - - - monomer-trimer model

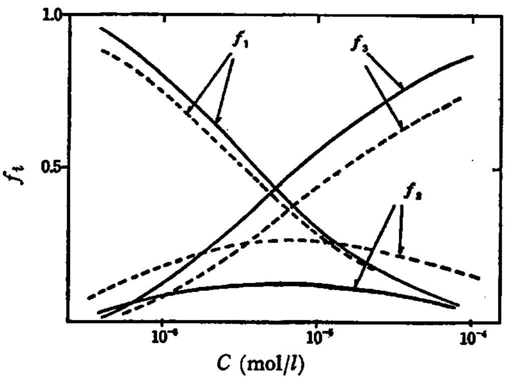

Fig. 2. Mole fractions of polymers *vs*. dye concentration (Benzopurprine 4B). ($f_i = iC_i/C$)
—— at salt concentration of 20 mmol/*l*
- - - - at salt concentration of 40 mmol/*l*

The deviations of the twenty models including all or a part of the monomer to heptamer at a salt concentration of 80 mmol/*l* are also compared. The monomer-tetramer-pentamer-hexamer-heptamer, the monomer-hexamer-heptamer, and the monomer-pentamer-hexamer-heptamer models may be preferable from the point of view of statistical analysis. The parameters of these models are also shown in Table 4.

TABLE 4. THE AGGREGATION PARAMETERS OF BENZOPURPRINE 4B AT SALT CONCENTRATION OF 80 mmol/*l*

	1+5	1+6	1+7	1+2+3+4	1+2+3+4+5	1+2+3+4+5+6+7
$\varepsilon_1\times10^{-5}$	0.480	0.478	0.478	0.503	0.501	0.500
$\bar{\varepsilon}_2\times10^{-5}$	—	—	—	0.349	0.350	0.352
$\bar{\varepsilon}_3\times10^{-5}$	—	—	—	0.347	0.360	0.380
$\bar{\varepsilon}_4\times10^{-5}$	—	—	—	0.350	0.365	0.358
$\bar{\varepsilon}_5\times10^{-5}$	0.347	—	—	—	0.333	0.340
$\bar{\varepsilon}_6\times10^{-5}$	—	0.353	—	—	—	0.352
$\bar{\varepsilon}_7\times10^{-5}$	—	—	—	—	—	0.347
$K_2\times10^{-5}$	—	—	—	0.6	0.6	0.6
$K_3\times10^{-10}$	—	—	—	6.2	6.2	6.2
$K_4\times10^{-15}$	—	—	—	3.0	3.0	3.0
$K_5\times10^{-20}$	15.7	—	—	—	15.8	15.7
$K_6\times10^{-25}$	—	93.0	—	—	—	93.1
$K_7\times10^{-30}$	—	—	432.2	—	—	432.8
Mean deviation (%)	1.3	1.3	1.3	1.7	1.7	1.6

	1+4+5	1+4+5+6	1+4+5+6+7	1+5+6	1+5+6+7	1+6+7
$\varepsilon_1\times10^{-5}$	0.479	0.480	0.481	0.479	0.481	0.479
$\varepsilon_2\times10^{-5}$	—	—	—	—	—	—
$\varepsilon_3\times10^{-5}$	—	—	—	—	—	—
$\varepsilon_4\times10^{-5}$	0.363	0.360	0.360	—	—	—
$\varepsilon_5\times10^{-5}$	0.345	0.345	0.436	0.346	0.346	—
$\varepsilon_6\times10^{-5}$	—	0.360	0.364	0.360	0.363	0.362
$\varepsilon_7\times10^{-5}$	—	—	0.363	—	0.361	0.359
$K_2\times10^{-5}$	—	—	—	—	—	—
$K_3\times10^{-10}$	—	—	—	—	—	—
$K_4\times10^{-15}$	3.0	3.0	—	—	—	—
$K_5\times10^{-20}$	15.7	15.7	15.7	15.7	15.7	—
$K_6\times10^{-25}$	—	92.9	93.0	92.9	93.0	93.0
$K_7\times10^{-30}$	—	—	431.9	—	431.9	432.0
Mean deviation (%)	1.3	1.4	1.5	1.3	1.5	1.4

TABLE 5. THE EXTINCTION COEFFICIENTS PER MOLECULE OF AGGREGATE (Benzopurprine 4B)

	NaCl concentration		
$\bar{\varepsilon}_n$	20 mmol/*l*	40 mmol/*l*	80 mmol/*l*
ε_1	0.50	0.50	0.48
$\bar{\varepsilon}_2$	0.43	0.36	—
$\bar{\varepsilon}_3$	0.43	0.42	—
$\bar{\varepsilon}_4$	0.42	0.43	0.36
$\bar{\varepsilon}_5$	—	—	0.35
$\bar{\varepsilon}_6$	—	—	0.37
$\bar{\varepsilon}_7$	—	—	0.36

Thus, it may be concluded that Benzopurprine 4B tends to form higher aggregates in more concentrated salt solutions. Further, it is noteworthy that the extinction coefficients per molecule of aggregates are all approximately the same (Table 5), and that the logalism of K_n increases in arithmetical progression (Fig. 3); that is,

$$\log K_n = 5.3(n-1)^{*5}$$

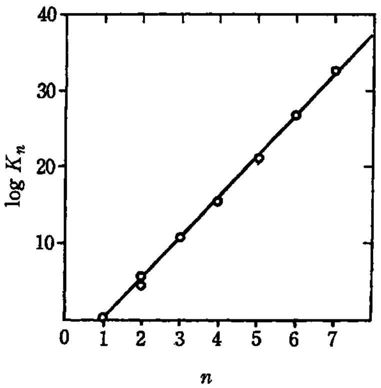

Fig. 3. Plot of log K_n *vs.* n (Benzopurprine 4B).

Alexander and Stacey observed the formation of the aggregation of Benzopurprine 4B by the light-scattering method; they estimated the degree of aggregation ($n>6$) in solutions of above 10^{-4} mol/*l* dye and above 10 mmol/*l* NaCl.[10] Table 6 shows that the dye did not scatter light below 10^{-4} mol/*l* dye and 20 mmol/*l* or 40mmol/*l* salt, but that it did scat-

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[*5] This may suggest the constancy of the molar free energy of aggregation; the subject will be discussed further elsewhere.

TABLE 6. LIGHT SCATTERING DATA OF BENZOPURPRINE 4B

Concentration of the dye (mol/l)	Concentration of salt (mmol/l) 20	40	80		
	Scattering (τ)			Relative scattering* (τ/τ_0)×100	
				obs.	calc.
10^{-6}	0	0.1	0.2	0.4	0.2
10^{-5}	0.1	0.1	2.7	12	8
10^{-4}	0.1	1	44	100	100

*A value at dye concentration 10^{-4} mol/l are chosen as τ_0.

ter light markedly above 10^{-5} mol/l dye and 80 mmol/l salt.

It has been shown that the reduced scattering (C/τ) is in a linear relationship with the reciprocal of the molecular weight.[10] Thus:

$$\text{const.}\, n^2(dn/dC)^2(C/\tau) = \frac{1}{M} + B_c,$$

where $\tau = I_S/I_0$, and I_S denotes the intensity of the light scattered at a right angle to the incident beam. By supposing that each aggregate scatters light independently, that the interaction term (B_c) is negligible, and that the refractive index (n) may be taken to be nearly constant, the scattering may be approxmately represented by Eq. (15):

$$\tau = I_S/I_0 \backsim (\textstyle\sum i^2 f_i)CM_0, \qquad (15)$$

where the index, i, ranges over the polymers included, f_i is the molar fraction of the i-mer, and M_0 is the molecular weight of monomer. Then the relative scattering (τ/τ_0) can be written as:

$$\tau/\tau_0 = \frac{(\sum i^2 f_i)C}{(\sum i^2 f_i)_0 C_0}, \qquad (16)$$

where τ_0 denotes the scattering of the most concentrated solution. In the fifth and the sixth columns of Table 6, the observed relative scatterings are compared with that calculated by Eq. (16); the molar fractions of the aggregates were computed by the use of the parameters of the monomer-hexamer-hpetamer model.

(2) **Benzopurprine 4B in an Alcoholic Solution.** The plots of the absorptivities against the log C of Benzopurprine 4B in an alcoholic solution were not sigmoid, but in an L shape. This means that the aggregation numbers and or formation constants are very large. If n is taken to be very large, Eq. (6) can be rewritten as Eq. (6′):

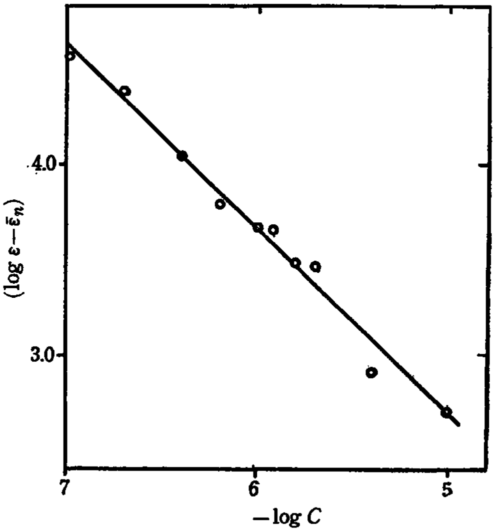

Fig. 4. Plot of $\log(\varepsilon-\bar{\varepsilon}_n)$ vs. $\log C$ in 90% n-butanol aqueous solution (Benzopurprine 4B). ($\bar{\varepsilon}_n = 5.25\times10^4$)

$$\log(\varepsilon-\bar{\varepsilon}_n) = -\frac{n-1}{n}(\log C + \log\alpha) \qquad (6')$$

Thus, a plot of $\log(\varepsilon-\bar{\varepsilon}_n)$ vs. $\log C$ gives a straight line with a slope of $-(n-1)/n$, near to -1, and an intercept of $[-(n-1)/n]\log\alpha$. As a typical example, Fig. 4 illustrates the aggregation in a 90% n-butanol aqueous solution in a high polymer ($n \doteqdot 30$). However, the equilibrium between the monomer and a single higher polymer may not be natural.

All from the monomer to the n-mer can be included, if it is assumed that all the absorptivities per molecule of n-mer's, except for the monomer, are identical, and that $K_n = K^{n-1}$. Then we have Eqs. (18) and (19):

$$C = \sum_i ik^{i-1}C_1{}^i \qquad (17)$$

$$C = \varepsilon_1 C_1 + \bar{\varepsilon}_n \sum_i iK^{i-1}C_1{}^i \qquad (18)$$

By combining Eq. (17) with Eq. (18), we obtain:

$$C_1/C = \frac{\varepsilon-\bar{\varepsilon}_n}{\varepsilon_1-\bar{\varepsilon}_n}. \qquad (19)$$

The sum of the progression in Eq. (17) may be calculated as:

$$C = \frac{C_1\{1-(n+1)(kC_1)^n + n(kC_1)^{n+1}\}}{(1-kC_1)^2} \qquad (20)$$

If kC_1 is taken to be much larger than unity, Eq. (20) can be written as follows:

$$kC \doteqdot n(kC_1)^n \qquad (21)$$

By substituting Eq. (19) into Eq. (21), we

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[10] P. Alexander and K. A. Stacey, *Proc. Roy. Soc. A*, **212**, 274 (1952).

get Eq. (22).

$$\log(\varepsilon-\bar{\varepsilon}_n)= -\frac{n-1}{n}(\log C+\log(\varepsilon_1-\bar{\varepsilon}_n)^n k^{1-n}/n) \quad (22)$$

when $(n-1)/n$ is near to unity, Eq. (22) is identical with Eq. (6′). Thus, Eq. (22) can give a physical meaning of Eq. (6′), derived by the monomer - *n*-mer model. The aggregation number in an *n*-butyl alcoholic aqueous solution (80%) is obtained as 30 by the linear plots of $\log(\varepsilon-\bar{\varepsilon}_n)$ *vs.* $\log C$. In this case kC_1 calculated by Eq. (23) is much larger than unity, since $\log k(\varepsilon_1-\bar{\varepsilon}_n)^{-1}$ is calculated as 5.3, and $\log C(\varepsilon-\bar{\varepsilon}_n)$ has values ranging between −2.4 and −2.3[*6]

$$kC_1=k(\varepsilon_1-\bar{\varepsilon}_n)^{-1}C(\varepsilon-\bar{\varepsilon}_n) \quad (23)$$

(3) Sky Blue FF (C.I. Direct Blue 1) in Aqueous Salt and Alcoholic Solutions. Sky Blue FF aggregates in polymer form not more than in trimer form in an aqueous salt solution. The parameters are compared in Tables 7, 8 and 9.

TABLE 7. PARAMETERS OF SKY BLUE FF IN AQUEOUS SALT SOLUTION (20 mmol/*l*)

Polymers included	2	3	2+3
$\varepsilon_1\times10^{-5}$	0.85 (0.843)	0.85 (0.844)	0.850 (0.855)
$\varepsilon_2\times10^{-5}$	1.46 (1.454)	—	1.460 (1.483)
$\varepsilon_3\times10^{-5}$	—	2.31 (2.257)	2.31 (2.258)
$K_2\times10^{-5}$	0.658 (0.658)	—	0.658 (0.657)
$K_3\times10^{-10}$	—	4.07 (4.062)	4.07 (4.060)
Mean deviation (%)	1.04 (0.85)	1.63 (1.09)	1.27 (1.17)

TABLE 8. PARAMETERS OF SKY BLUE FF IN AQUEOUS SALT SOLUTION (40 mmol/*l*)

Polymers included	2	3	2+3
$\varepsilon_1\times10^{-5}$	0.83 (0.830)	0.83 (0.830)	0.83 (0.835)
$\varepsilon_2\times10^{-5}$	1.38 (1.380)	—	1.38 (1.380)
$\varepsilon_3\times10^{-5}$	—	2.22 (2.191)	2.22 (2.216)
$K_2\times10^{-5}$	0.32 (0.320)	—	0.32 (0.320)
$K_3\times10^{-10}$	—	1.03 (1.026)	1.03 (1.026)
Mean deviation (%)	0.47 (0.47)	0.86 (0.65)	0.66 (0.63)

TABLE 9. PARAMETERS OF SKY BLUE FF IN AQUEOUS SALT SOLUTION (80 mmol/*l*)

Polymers included	2	3	2+3
$\varepsilon_1\times10^{-5}$	0.82 (0.811)	0.82 (0.810)	0.82 (0.822)
$\varepsilon_2\times10^{-5}$	1.36 (1.361)	—	1.36 (1.370)
$\varepsilon_3\times10^{-5}$	—	2.19 (2.136)	2.19 (2.139)
$K_2\times10^{-5}$	0.24 (0.243)	—	0.24 (0.242)
$K_3\times10^{-10}$	—	0.54 (0.538)	0.54 (0.538)
Mean deviation (%)	1.21 (1.14)	1.68 (1.18)	1.53 (1.36)

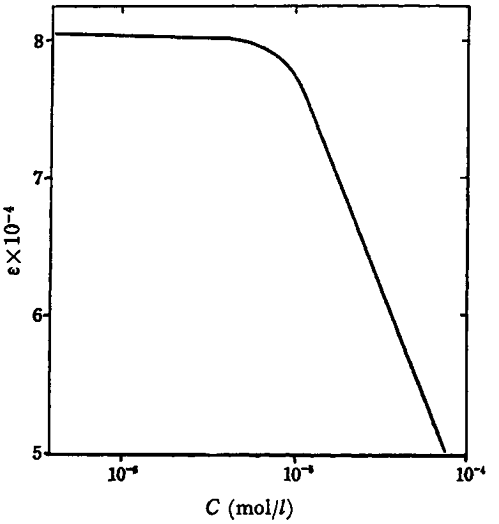

Fig. 5. Change of molar absorptivity of Sky Blue FF with the concentration in butanolic solution.

In aqueous ethanolic solutions the molar absorptivity did not change in a range of the dye concentrations between 10^{-6} and 10^{-4} mol/*l*. However, we cannot decide from the spectroscopic measurements alone whether Sky Blue FF in aqueous solutions is present in the monomeric or the polymeric state.

On the other hand, the dye in aqueous *n*-butanolic solutions aggregated suddenly into a very high polymer, or into particles, above 10^{-5} mol/*l* (Fig. 5). This fact might be connected with the dyeing behavior of the dye in this solvent, but more work is required in order to elucidate this connection.

Experimental

The dyes have been purified several times by the Robinson-Mill method, until no variation in the

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[*6] If $kC_1 \ll 1$, which is the case in an aqueous ethanolic solution, then :

$$\sqrt{\varepsilon-\bar{\varepsilon}_n}=\sqrt{\varepsilon_1-\bar{\varepsilon}_n}-\frac{k}{\sqrt{\varepsilon_1-\bar{\varepsilon}_n}}C(\varepsilon-\bar{\varepsilon}_n).$$

Hence, k and $(\varepsilon_1-\bar{\varepsilon}_n)$ can be obtained from a plot of $\sqrt{\varepsilon-\bar{\varepsilon}_n}$ *vs.* $C(\varepsilon-\bar{\varepsilon}_n)$.

absorption spectra was found. All the dye solutions were allowed to stand for 24 hr at 30°C after having been prepared, and their absorption spectra were measured at the same temperature.

Computations by the minimum deviation method were carried out on a HITAC 5020 E computer (the Tokyo University computation Center). The computation program used in these calculations was similar to that by Lepse.[11]

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[11] K. B. Wiberg, "Computer Programming for Chemists," Benjamin (1965), p. 185.