Note on the Polymerization of Dyes in Solution

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1. Introduction

Many investigations have been made on the aggregation of dye molecules or ions in aqueous solution, and it seems clear that some dyes form dimers and polymers in suitable conditions. For example, thionine, methylene blue, toluidine blue[1-3], rhodamine 6G[4], pyronine G[5] form dimers while acridine orange[6] forms dimer and higher polymers. Even in organic solvents dye molecules can often exist in a certain aggregated state. For example, Lewis et al.[7] reported that methylene blue in EPA at low temperature (liquid nitrogen) shows dimerization and polymerization of higher degree. Further, according to Zanker[8,9], acridine orange forms a definite polymer at low temperature in a mixed solvent of alcohol and ether.

Some qualitative discussions on the factors determining the association and also on the mechanism of spectral shift caused by association, have been made heretofore. For example, Rabinowitch and Epstein[1] have ascribed the cause of association to a large dispersion force between dye ions which have strong absorption bands in the visible spectral region.

Förster[10] has proposed a classical model for the interpretation of spectral shift caused by association. According to his theory, the dye ions in dimerized state take the plane parallel configuration, in which the dispersion force between pair of each dye ion is the largest. In this configuration, the electron oscillators of dye ions couple with each other, and there result symmetric and antisymmetric combinations, of which the former with a larger frequency than that of the original one can appear as absorption.

It is questioned, however, whether the complicated nature of the dimerization or polymerization of dyes in solution can well be comprehended by such a simplified interpretation.

As to a delicate aspect of dimerization or polymerization, some remarks were made previously by the present author in relation to the mechanism of metachromasy phenomenon[11].

Recently, Levshin has studied the effect of concentration on the optical properties of solution of acridine derivatives such as monoamino- and diamino-acridine[12-14]. He insists that the concentration effect is due to the dimerization of these molecules.

The present author has also investigated the concentration effect on the absorption spectra of 2,8-diaminoacridine (DAA) and 2,8-bisdimethylaminoacridine (BDAA) in various organic solvents. By the analysis of absorption spectrum according to the method of Zanker[8], it has been established that, contrary to Levshin's opinion, these molecules form higher polymers very easily in some organic solvents. It has also been confirmed that, the influence of solvent and of a slight difference in molecular structure between DAA and BDAA is very prominent in the phenomenon.

Levshin did not make any remarks about these points.

The object of the present paper is to report about these points with some discussions on the mechanism of dimerization or polymerization.

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[1] E. Rabinowitch, and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).

[2] S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942).

[3] S. E. Sheppard and A. L. Geddes, *J. Am. Chem. Soc.*, **66**, 1995, 2003 (1944).

[4] V L. Levshin, *Acta Physicochim. USSR.*, **1**, 685 (1935); **4**, 221, (1936).

[5] N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **4C**, 167 (1953); M. Koizumi and N. Mataga, This Bulletin, **27**, 194 (1954).

[6] V. Zanker, *Z. Physikal. Chem.* **199**, 225 (1952).

[7] G. N. Lewis et al., *J. Am. Chem. Soc.*, **65**, 1150 (1943).

[8] V. Zanker. *Z. Physikal. Chem.*, **200**, 250 (1952).

[9] G. Scheibe and V. Zanker, *Z. Physik*, **133**, 244 (1952).

[10] Th. Förster, "Fluoreszenz organischer Verbindungen", Gottingen, Vandenhoech and Ruprecht (1951), p. 254.

[11] N. Mataga, *J. Inst. Polytech. Osaka City Univ.*, **4C**, 189 (1953).

[12] V. L. Levshin, *Doklad. Akad. Nauk SSSR*, **96**, 473 (1954).

[13] V. L. Levshin, *Zhur. Eksptl. i. Teoret. Fiz.*, **28**, 201 (1954).

[14] V. L. Levshin, ibid., **28**, 213 (1955).

2. Experimental

Apparatus. — Absorption spectra were measured with Beckman spectrophotometer model D. U. and the lengths of cells used were 10, 1, 0.1 and 0.007 cm. Using these cells, measurement in the concentration range from 10^{-6} to 10^{-2} mol./l. was possible.

Reagent.—DAA was the same sample as described elsewhere[15]. BDAA was purified by the method of Moudgill[16] and Biehringer[17]. Excess of sodium hydroxide was added to the aqueous solution of acridine orange (Zinc Salt of BDAA) which was kindly supplied by Sumitomo Chemical Co. Ltd.; BDAA was extracted with ethanol, and purified by repeated recrystallization from ethanol-water mixture.

Methanol was refluxed with calcium oxide and distilled. Ethanol was also refluxed with calcium oxide and distilled fractionally. Extra pure-grade butanol was used without further purification. Purified acrylonitrile was kindly supplied by Mr. K. Nakatsuka of this Institute.

Acetone was refluxed with potassium permanganate and, after being dried over potassium carbonate, distilled fractionally. Extra pure grade pyridine was dried over sodium hydroxide and distilled before use.

3. Experimental Results

Zanker[18] has systematized the electronic spectra of nitrogen heterocycles in analogy to those of aromatic hydrocarbons, using Platt's perimeter model[19]. According to his classification, the longest wave length bands of these molecules are due to the transition to ^1L_a. Because of the light absorption by solvent, the observation of shorter wave length bands is not possible. Therefore only the effect of concentration on the ^1L_a band was studied. Some examples of the concentration dependence of absorption spectra are shown in Figs. 1-5.

It is clear from these spectral changes that there are only two molecular species

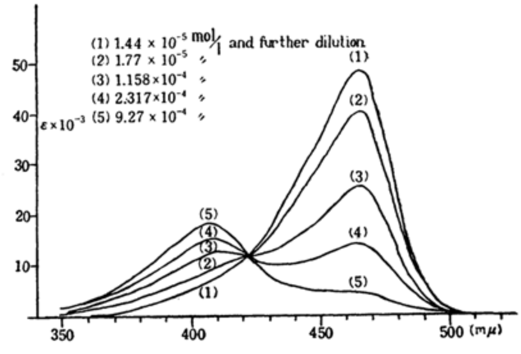

Fig. 1. DAA in pyridine

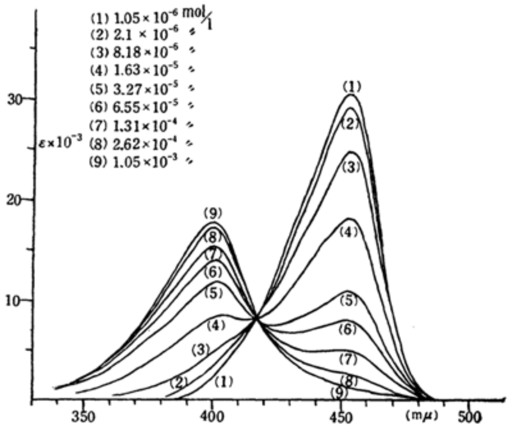

Fig. 2. DAA in acrylonitrile

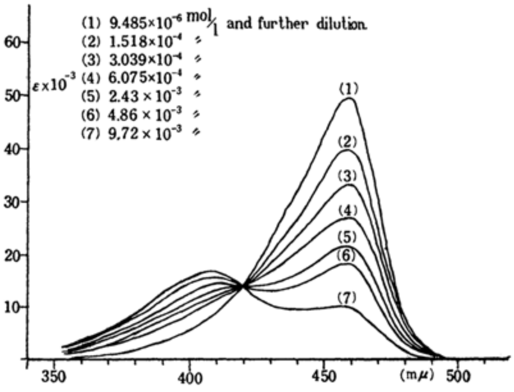

Fig. 3. DAA in ethanol

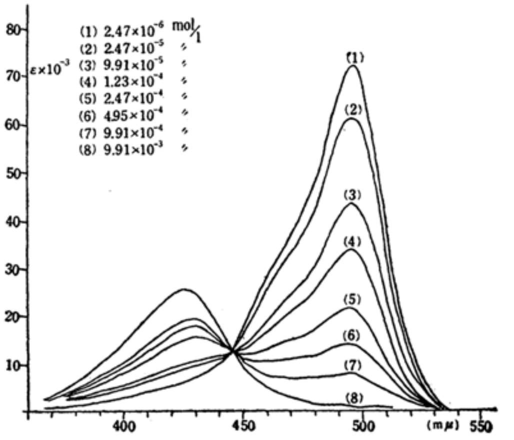

Fig. 4. BDAA in acrylonitrile

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15) N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 373 (1956).

16) K. L. Moudgill, *J. Chem. Soc.*, **1922**, 1508.

17) J. Biehringer, *J. Praktisch. Chem.*, **57**, 217 (1896).

18) V. Zanker, *Z. Physikal. Chem.*, *N. F.*, **2**, 52 (1954).

19) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949); H. B Klevens and J. R. Platt, ibid., **17**, 470 (1949).

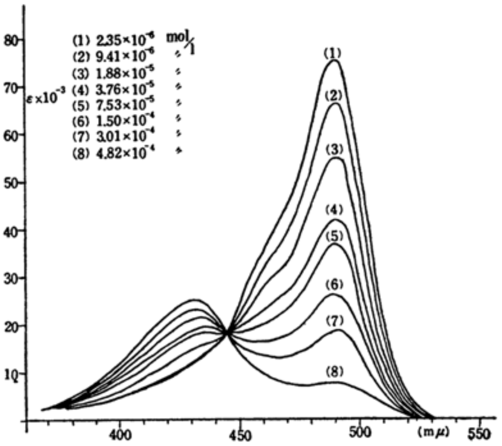


Fig. 5. BDAA in ethanol

in equilibrium, i. e., monomer and polymer. For the equilibrium between monomer and polymer of nth degree, the equilibrium constant of association is expressed as:

$$K=\frac{x}{nc_0^{\,n-1}(1-x)^n} \tag{1}$$

where, $(1-x)$ is the fraction of monomer against the total quantity as monomer and c_0 is the analytical concentration of dye.

The apparent extinction coefficient ε at a definite wave length can be expressed by means of ε^n and ε^m which are the extinction coefficients of polymer and monomer, respectively, at the same wave length.

$$\varepsilon=\frac{1}{n}x\varepsilon^n+(1-x)\varepsilon^m \tag{2}$$

From (1) and (2), we obtain the following equations.

$$\log c_0\left(1-\frac{\varepsilon}{\varepsilon^m}\right)=\log(C\cdot K)+n\log c_0\left(\frac{\varepsilon}{\varepsilon^m}-\frac{\varepsilon^n}{n\varepsilon^m}\right) \tag{3}$$

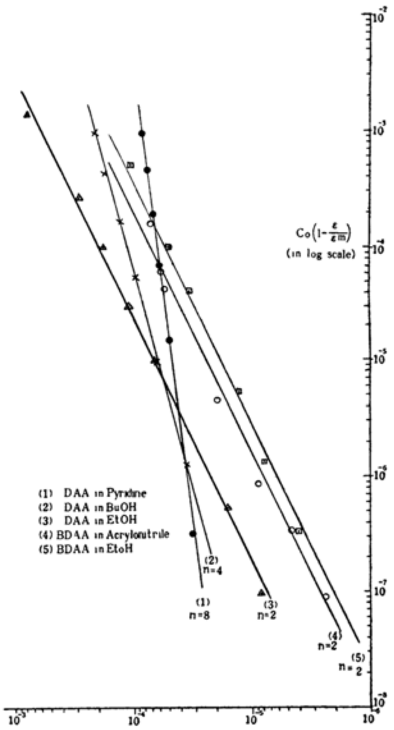
$$C=\frac{1}{n^n\left(n-\dfrac{\varepsilon^n}{\varepsilon^m}\right)^{n-1}}$$

In the first approximation, we can neglect $\dfrac{\varepsilon^n}{n\varepsilon^m}$ as compared with $\dfrac{\varepsilon}{\varepsilon^m}$

$$\log c_0\left(1-\frac{\varepsilon}{\varepsilon^m}\right)=\log(C\cdot K)+n\log c_0\left(\frac{\varepsilon}{\varepsilon^m}\right) \tag{4}$$

By means of (4), we can determine n, then using (3) we can evaluate K.

Some examples of $\log c_0\left(1-\dfrac{\varepsilon}{\varepsilon^m}\right)\sim\log c_0\left(\dfrac{\varepsilon}{\varepsilon^m}-\dfrac{\varepsilon^n}{n\varepsilon^m}\right)$ plots are shown in Fig. 6. It is clear from these plots, that there is only monomer-polymer equilibrium, in contradistinction to the case of acridine orange in aqueous solution⁶⁾ where polymerization proceeds stepwise, i. e., monomer-dimer equilibrium exists in relatively dilute solution, and dimer-tetramer equilibrium is established in a highly concentrated solution.



$C_0\left(\dfrac{\varepsilon}{\varepsilon^m}-\dfrac{\varepsilon^n}{n\varepsilon^m}\right)$ (in log scale)

Fig. 6. $\log C_0\left(1-\dfrac{\varepsilon}{\varepsilon^m}\right)\sim\log C_0\left(\dfrac{\varepsilon}{\varepsilon^m}-\dfrac{\varepsilon}{n\varepsilon^m}\right)$ relations for DAA and BDAA.

4. Discussion

The results obtained are collected in Tables I and II for DAA and BDAA, respectively.

As Levshin has pointed out¹³⁾, the dimerization or polymerization tendency has no correlation with refractive index, dielectric constant, or dipole moment of the solvent used.

TABLE I

COLLECTED DATA FOR DAA

Solvent	Pyridine	Acrylonitrile	Acetone	BuOH	EtOH	H_2O
Equilibrium constant	1.2×10^{43}	1.6×10^{19}	3.0×10^{20}	9.2×10^{15}	1.7×10^{4}	2.7×10^{3}
K_n^T	K_8^{283}	K_4^{283}	K_4^{283}	K_4^{283}	K_2^{283}	K_2^{283}
$\delta\tilde{\nu}$ (kcal.)	8.7	8.4	8.1	8.2	7.8	1.9
$\bar{f}_{\text{monomer}}$[a]	0.74	0.37	0.44	0.66	0.66	0.33
$f^{v.}_{\text{monomer}}$[a]	0.36	0.21	0.27	0.38	0.40	0.21

a) $\bar{f}_{\text{monomer}}=\dfrac{n}{N}\dfrac{c^2m}{\pi e^2}10^3\displaystyle\int_0^\infty\varepsilon(\tilde{\nu})\,d\tilde{\nu}=4.32\times10^{-9}\,n\int_0^\infty\varepsilon(\tilde{\nu})\,d\tilde{\nu}$

n: Refractive index of solvent

$\int_0^\infty\varepsilon(\tilde{\nu})\,d\tilde{\nu}$: Integrated absorption for monomeric band

$f^{v.}_{\text{monomer}}=\left(\dfrac{3}{n^2+2}\right)^2 f_{\text{monomer}}$

$\bar{f}$ and $f^{v.}$ are the oscillator strengths in solution and in vapor state, respectively. N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

TABLE II

COLLECTED DATA FOR BDAA

Solvent	Acrylonitrile	Acetone	BuOH	EtOH	MeOH
Equilibrium constant	$1.2+10^{5}$	3.2×10^{6}	1.3×10^{5}	1.9×10^{5}	4.1×10^{4}
K_n^T	K_2^{293}	K_2^{295}	K_2^{294}	K_2^{294}	K_2^{301}
$\delta\tilde{\nu}$ (kcal.)	9.4	8.4	8.1	8.1	7.6
$\bar{f}_{\text{monomer}}$	0.93	0.68	0.83	1.01	0.84
$f^{v.}_{\text{monomer}}$	0.54	0.42	0.47	0.61	0.53

TABLE III

Dye ions	Thionine[a]	Methylene blue[a]	Rhodamine 6G[b]	Pyronine G[c]	Acridine orange[d]	Trypaflavine[e]	DAA
$\delta\tilde{\nu}$ (kcal.)	3.4	4.1	3.4	3.3	3.4	2.0	1.9
$\bar{f}_{\text{monomer}}$	0.77	0.60	0.72	0.13	0.82	0.73	0.33
$f^{v.}_{\text{monomer}}$	0.48	0.38	0.45	0.08	0.52	0.46	0.21

a) Ref. 1), b) Ref. 4), c) Ref. 5), d) Ref. 6),
e) Measured by the present writer.

An analogous idea to that of Förster[10], but in wave mechanical form was developed by Mori[20] for the case of dimerization, assuming a simplified model of dipole-dipole interaction similar to that used in the calculation of dispersion force, and the treatment was extended to the case of polymer[21].

This has its analogy in the theory of Davydov splitting or exciton migration.

According to it, the blue shift due to dimerization is expressed as follows:

$$hc\Delta\sigma=\frac{1}{R^3}(\vec{\mu}^{\,1}_{eg}\mid\vec{\mu}^{\,2}_{eg}) \tag{5}$$

where $\Delta\sigma$ is the wave number shift, R is the distance between dye molecules which are in plane-parallel configuration, and $\vec{\mu}_{eg}$ is the transition dipole of monomeric dye molecule, and in this configuration, $(\vec{\mu}^{\,1}_{eg}\mid\vec{\mu}^{\,2}_{eg})>0$. If the association is due to the dispersion force between monomers and the spectral shift is determined by equation (5), then the association tendency and the magnitude of spectral shift should depend on the oscillator strength of monomeric band.

As seen from Table III, however, the spectral shifts of various dye ions in aqueous solution have no correlation with their oscillator strengths of monomeric bands.

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[20] Y. Mori, Symposium on π-electronic state, *Chem. Soc. Japan*, 1955.

[21] N. Mataga, Unpublished.

Moreover, it is clear from Tables I and II, that the polymerization tendencies of DAA and BDAA in organic solvents have no dependence on their oscillator strengths of monomeric bands. For the association to occur it might be necessary that the oscillator strength of monomeric band be fairy large, because, for example, the integrated absorption $\int_0^\infty \varepsilon(\tilde{\nu})d\tilde{\nu}$ of ${}^1L_a$ band of acridine is nearly 10^7 in its order of magnitude, whereas it is approximately 10^8 for DAA and BDAA, and we could not observe any concentration dependence of spectra of acridine in various solvents such as used for DAA and BDAA, in the concentration range from 10^{-5} to 10^{-3} mol./l.

It seems clear, however, that the association is very sensitive to the solvent used, and also it depends remarkably on the slight difference of molecular structures of dye molecules.

By inspection of Tables I and II, we see that the association tendency of DAA is greater than that of BDAA. Further, it is remarkable, that in pyridine, DAA forms octamer, whereas BDAA shows no associating tendency. Hydrogen bonding of solvent molecules with amino groups of DAA, might play some important role in the association.

Summary

The effect of concentration on the absorption spectra of DAA and BDAA in various organic solvents was studied in the concentration range from 10^{-6} to 10^{-2} mol./l. Contrary to Levshin's opinion, DAA forms polymers higher than dimer very easily in some organic solvents, and the association tendency of DAA is greater than that of BDAA.

Further, the association of these molecules is very sensitive to the solvents used. The association tendency and the spectral shift due to dimerization or polymerization have no correlation with the oscillator strengths of monomeric bands of these molecules, and this is true also for the various dye ions in aqueous solution.

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