Influence of the Addition of High Molecular Electrolytes upon the Absorption Spectra and Fluorescence of Organic Dyestuffs. II.

By Masao KOIZUMI and Noboru MATAGA

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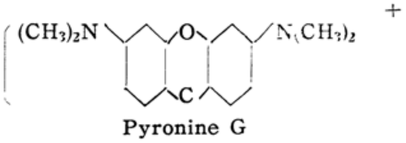
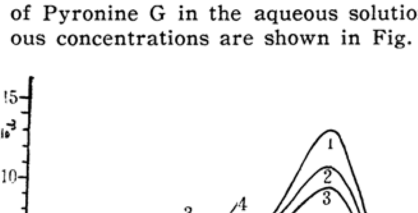
In the second paper1) of our series of physicochemical studies of organic dyestuffs**, the influence or addition of K-polyvinylsulfate (PVSK) upon the absorption spectra and fluorescence of Rhodmaine 6G was reported, and the results were explained almost quantitatively as due to the change of aggregation of dye ions, which is caused by the accumulation of the latter in the neighbourhood of PVSK. Now in the course of our extensive study of the influence of PVSK upon various basic dyes, which was continued since then, we have found another interesting example which can be comprehended almost quantitatively as due to the change of aggregation of dye ions. It is Pyronine G, which belongs to Xanthen dyestuffs and its structure is somewhat more simple than Rhodamine 6G. In this case a new metachromatic band appears by the addition of PVSK, in contrast to the case of Rhodamine 6G, and yet the main features of the change of absorption spectrum are so simple and orderly that the quantitative treatment is possible. Pyronine G—PVSK system may be regarded as another ideal case of metachromasy which can be interpreted on the basis of the change of aggregation of dye ions.



Pyronine G



Rhodamine 6G

Experimental

a) Some examples of the absorption spectra of Pyronine G in the aqueous solution at various concentrations are shown in Fig. 1.

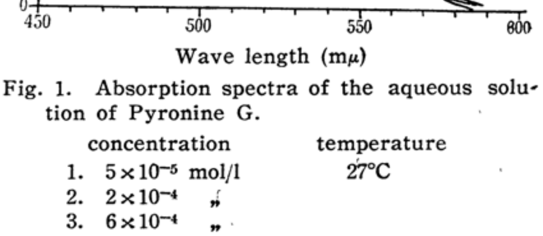


Fig. 1. Absorption spectra of the aqueous solution of Pyronine G.

	concentration	temperature
1.	5×10^{-5} mol/l	27°C
2.	2×10^{-4}	"
3.	6×10^{-4}	"
4.	2×10^{-3}	"

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* Physicochemical Studies of Organic Dyestuffs in relation to Photochemistry. III.

**) The paper will, hereafter, be refered to as Part I of "Influence of the addition of high molecular electrolytes upon the absorption spectra and fluorescence of organic dyestuffs".

1) M. Koizumi and N. Mataga, This Bulletin 26, 165 (1953); See also: N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **3**, 21 (1952).

The absorption curve has two maxima at 545 mμ and 512.5 mμ. The former is prominent in the region of low concentration, while the latter gradually grows with the increase of concentration. Thus two maxima 545 and 512.5 mμ are expected to belong respectively to monomer (α-band) and dimer (β-band), an equilibrium existing between the two, as in the case of Rhodamine 6G[1,2,3,4]. (The equilibrium constant of dimerization was calculated to be 6.38×10^{-4} at 27°C.).

b) The effect of addition of PVSK is characteristic in its simplicity. Up to 2×10^{-4} mol./1. of dye the concentration, no change is produced in the spectrum. If the concentration of dye is a little above 4×10^{-4} mol./1. the absorption curve changes its shape with the addition of PVSK. Thus both α- and β-bands gradually decline apparently in a parallel way and a new metachromatic band appears at the position 800 Å shorter than the α-band, and it gradually grows with the addition of more PVSK. When the concentration of added PVSK reaches a certain critical concentration, however, the metachromatic band begins to decline accompanied with the rise of α- and β-band. until the shape of the curve coincides almost completely with that of the aqueous solution without PVSK. But as the concentration of dye increases, the phenomenon of recovery commences at a larger concentration of PVSK, and at last, when the dye concentration is about 2×10^{-3} mol./1. the recovery occurs only very slightly. (See Fig. 2)

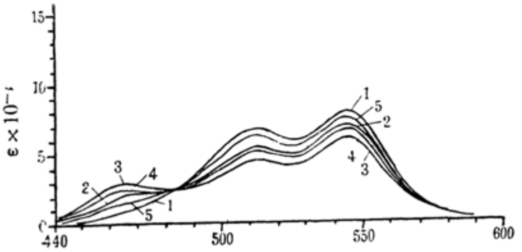

Fig. 2. Change of absorption spectra of Pyronine G by the addition of PVSK. (Dye conc. 8×10^{-4} mol./1.)

	PVSK	temperature
1.	0 and 1000 (7.56×10^{-3}gr/cc)	27°C
2.	5	..
3.	10	..
4.	50	..
5.	500	..

If one compares the above result with that of Rhodamine 6G[1], the chief points of difference are the rise and fall of α- and β-band occuring apparently in a parallel way. and the appearance of a new metachromatic band. As regards to the phenomenon of recovery, it is qualitatively similar to that in the case of Rhodamine 6G, but it is more elegant and complete in the region of low concentration of dye. It may be worthy to add that the positions of α-, β- and metachromatic band are invariable during the whole change.

Discussion

Let us consider the mechanism of metachromasy in the present case on the ground of the following experimental results.

1) Below 2×10^{-4} mol./1. of the dye concentration, no change is produced in the absorption spectrum, even if large excess of PVSK is added.

2) In the case of dye concentration a little above 4×10^{-4} mol./1. the addition of PVSK produces a metachromatic band with the fall of α- and β-band, but with the excess of added PVSK the spectra become similar to that of pure aqueous solution.

3) When the concentration of dye is increased furthermore, the change of absorption spectra, including the appearance of a metachromatic band, becomes more prominent and at the same time, the recovery is retarded and quite reduced.

To explain the result (1), we must recognize one of the following two situations.

A) The change of the electronic state of dye ions may be produced by their interaction with the electrolyte ions, but in the region of low concentration of dye, the number of interacted molecules, is so small that it cannot be observed as any change in spectra (It may alternatively be said that there is approximately no adsorption, provided that the model of adsorption[1] is adopted.)

B) Dye ions are adsorbed on the high molecular substance, but neither the equilibrium between monomer and dimer, nor the optical properties of both monomer and dimer in relation to the absorption, spectrum, are affected by the adsorption.

Of the two possibilities mentioned above, A) cannot be reconciled with the facts (2) and (3) consistently. Thus the fact (3) might be attributed to the increase of adsorption (though small), but as long as one recognizes A), the quantity of adsorbed dye is so small as compared with the added high molecular substance, that the conditions around the adsorbed dye ion cannot be expected to be affected much by the addition of excess PVSK. Therefore, the fact (2) cannot be explained along this line, and some additional assumption is necessary. For example, if the structure of high molecular substance changes, in the region of its high concentra-

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[2] V. L. Levshin, *Acta Physicochim. U. R. S. S.* **1**, 684 (1935).

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

[4] S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942); S. E. Sheppard and A. L. Geddes, *J. Am. Chem, Soc.*, **66**, 1995, 2003 (1944).

tion, so remarkably in such a manner that it cannot adsorb the dye ions any longer, then the fact (2) could be explained. But this is also improbable in view of the fact (3) and also of the equilibrium dialysis experiment of Levine and Schubert[5].

The conclusion is, therefore, that one must assume the situation B). According to B), the fact 3) can be interpreted, for example, as due to the formation of a multiple associate of dye ions in the region of high concentration of dyes, and the result 2) can naturally be expected since the concentration of adsorbed dye ions decreases with the addition of an excess quantity of PVSK.

On the ground of the above qualitative deduction, it is much probable to attribute the change of absorption spectra of Pyronine-G, induced by the addition of PVSK, to a change of aggregation of dye ions.

Let us criticize this idea more quantitatively in the region of small concentration of dye, where the quantitative treatment is possible. Assume that in a certain range of the concentration of adsorbed dye ions, there is formed a new molecular species other than normal monomer and dimer, which produces a metachromatic band and it does not participate in monomer-dimer association equilibrium. (It may be added that this molecular species is probably a multiple associate but the calculation below does not necessarily require to be so).

Molar extinction coefficients at the position of α- and β-maximum in the pure aqueous solution are correlated with the experimentally obtained extinction coefficient λ by the following equations.

$$\left.\begin{array}{l}\lambda_m = C_0\varepsilon_m \\ \lambda_d = C_0\varepsilon_d\end{array}\right\} \qquad (1)$$

where C_0 is the analytical concentration of dye (mol./l.) and ε_m, ε_d are the molar extinction coefficients at α- and β-maxima, respectively.

Now, when PVSK is added enough for a new molecular species to appear, the concentration of dye ions participating in association equilibrium may be reduced to some extent. If the reduced concentration be put as $(C_0-\varDelta C_0)$, then the molecular extinction coefficient ε_m', ε_d' at the present condition ought to be given as follows:

$$\left.\begin{array}{l}\lambda_m' = C_0\varepsilon_m' = (C_0 = \varDelta C_0)\varepsilon_m \\ \lambda_d' = C_0\varepsilon_d' = (C_0 - \varDelta C_0)\varepsilon_d\end{array}\right\} \qquad (2)$$

It is to be added that the above relations (2) assume that a pure metachromatic band is negligible at the position of α- and β-maximum, which is very much plausible in view of the experimental results.

From (2), the following relations must hold.

$$\varepsilon_m' = \frac{(C_0-\varDelta C_0)}{C_0}\varepsilon_m, \quad \varepsilon_d' = \frac{(C_0-\varDelta C_0)}{C_0}\varepsilon_d \qquad (3)$$

$$\frac{\varepsilon_m'}{\varepsilon_d'} = \frac{\varepsilon_m}{\varepsilon_d}$$

Thus if one calculates and tabulates previously, $\frac{\varepsilon_m}{\varepsilon_d}$-values against various concentrations of dye from the spectrum of the pure aqueous solution, then by comparing the experimentally obtained $\frac{\varepsilon_m'}{\varepsilon_d'}$-value with the table, one can decide the value of $(C_0-\varDelta C_0)$ or $\varDelta C_0$.

The value of $\frac{(C_0-\varDelta C_0)}{C_0}\varepsilon_m$, obtained by the above procedure ought to coincide with ε_m' as long as the starting assumption is correct. The results of the calculation satisfy this requirement almost completely as shown in Table 1.

TABLE I

COMPARISON BETWEEN ε_m' AND $\frac{(C_0-\Delta C_0)}{C_0}\varepsilon_m$

a) Concentration of dye $C_0=8\times10^{-4}$ mol./l.

P*	0	1	5	10	50	100	500	1000
$\Delta C_0(\times10^4)$	0	0.1	1.6	2.0	1.4	1.4	0.1	0
ε_m'	8.0	7.95	7.0	6.1	6.7	7.1	7.6	7.8
ε_m	8.0	8.2	8.8	9.0	8.7	8.7	8.2	8.0
$\frac{(C_0-\Delta C_0)}{C_0}\frac{\varepsilon_m}{\varepsilon_m'}$	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0

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[5] A. Levine and M. Schubert, *J. Am. Chem. Soc.*, **74**, 5702 (1952).

b) Concentration of dye $C=10^{-3}$ mol./1.

P	0	1	5	10	50	100	500	1000
$\Delta C_0(\times 10^4)$	0	1.4	2.4	3.4	3.8	3.9		1.8
ε_m'	7.7	8.2	6.75	5.7	4.5	4.9		6.3
ε_m	7.7	8.0	8.7	8.8	8.9	8.94		8.0
$\frac{(C_0-\Delta C_0)}{C_0}\frac{\varepsilon_m}{\varepsilon_m'}$	1.0	0.8	0.97	1.0	1.2	1.1		1.0

* P: Quantity of PVSK added (Unit.: 7.56×10^{-6} g./cc.)

Thus it has been quantitatively proved that what produces a metachromatic band behaves as a new molecular species and lies outside monomer-dimer equilibrium. There scarcely remains any doubt that this new molecular species is polyassociate and is neither monomer nor dimer attached to PSVK in views of the qualitative discussion already stated. It is possible to discuss quantitatively other possibilities than the above one which is most probable, but the detailed discussion including them will be reported in Journ. Polytech. Osaka City University, with the full account of experimental results.

Institute of Polytechnics, Osaka City University, Osaka