Physicochemical Studies of Organic Dyestuffs in Relation to Photochemistry. II. Influence of the Addition of K-Polyvinylsulfate upon the Absorption Spectra and Fluorescence of Rhodamine 6G in Aqueous Solution

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Introduction

We have taken up the investigation of metachromasy, as the first step towards the study of the interaction between high polymers and organic dyes.

There are some experimental works reported on this phenomenon,⑴⑵⑶ but the general theory which is applicable to all cases has not yet been established; the phenomenon seems in general to be very complicated and perhaps may not be explained from a single view-point. Among various ideas proposed for the mechanism, the following two seem to be most noteworthy.

(1) According to the first idea, metachromasy is considered as a result of some change in the electronic structure of dye ion which is caused by the electrostatic interaction between high-molecular-weight electrolyte and dye ion.⑶

(2) According to the second idea, it is attributed to the change of aggregation of dye ions which results from the adsorption of the latter upon high polymers.⑴⑵

These two ideas do not, as we believe, contradict each other. There may exist some cases which can be comprehended simply by the first theory and others which can be explained only by the second theory. In general, however, there will be many cases which can be interpreted correctly only when both of the two theories are taken into account.

In the following discussion the above two cases will be called the ideal case (1) and case (2), respectively. For the systematic investigation of metachromasy, it is desirable, we believe, to search at first for such ideal cases which can be fully explained as case (1) or case (2). For this search, the following arguments might be of some help. If the metachromatic molecule has only one functional group and is of relatively low molecular weight, and the aqueous dye solution obeys Beer's law, then such a system may have a greater chance to be treated as the case (1). On the other hand, the case (2) may be found in those systems where the metachromatic molecule has more than two functional groups of weak nature, and the dye does not obey Beer's law.

Now the aqueous solution of Rhodamine 6 G shows, on one hand, only feeble metachromasy by the addition of K-Poly-vinylsulfate (P. V. S. K.),⑶ which is rather a strong metachromatic substance, while, on the other hand, some of the Rhodamine ions are in the dimerised state in the aqueous solution, the fraction of the dimer increasing with the concentration according to the mass action law.⑷ On the ground of these facts already reported by other investigators, we considered that Rhodamine 6 G-PVSK system might be treated as the case (2), and it has been confirmed to be the case by the present systematic study over a wide range of concentrations both of the dye and PVSK.

The purpose of this paper is to show how the change in the absorption spectra of the Rhodamine 6 G aqueous solution caused by the addition of PVSK can be interpreted quantitatively as the ideal case (2). In addition we will report some experimental results on the quenching of fluorescence of Rhodamine 6 G by PVSK, and will discuss them on the same ground.

Experimental

For the measurement of absorption spectra and the relative intensity of fluorescence, Beckman Spectrophotometer Model D. U. was used.

PVSK was obtained by the sulfonation of polyvinyl alcohol of which the polymerization

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(1) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**, 1212 (1945).

(2) L. Michaelis, *J. Phys. & Colloid* Chem., **54**, 1 (1950).

(3) Terayama, *Kagakuno Ryoiki*, **1**, 71 (1947).

(4) W. L. Levshin, *Acta Physicochim. U. R. S. S.*, **1**, 684 (1935).

degree was 1800. Two samples were prepared whose degrees of sulfonation were determined to be 61 % and 36 %.

The experimental results can be summarised as follows.

(a) The absorption spectrum of Rhodamine 6 G in aqueous solution has a peak at 526 $m\mu$ with a small shoulder at 500 $m\mu$ when dilute, while as the concentration increases, the latter grows gradually, the former reducing at the same time. This observation is the same as reported by other investigators and the peaks at 526 $m\mu$ and at 500 $m\mu$ are considered respectively to be due to the monomer (M-Band) and the dimer (D-Band).⁽⁴⁾

(b) The molar fluorescence intensity, F/C (where F is the intensity and C is the analytical concentration of dye in mol. mol./l.) remains constant from very dilute solution up to 5×10^{-6} mol/l., but beyond this value, it decreases monotonously with increasing concentration and approaches zero asymptotically.

(c) When PVSK is added step by step to the Rhodamine 6 G aqueous solution of a finite concentration, at first D-Band grows gradually accompanied with the reduction of M-Band, but when the quantity of the added PVSK reaches a certain critical value, then M-Band begins to grow again, though the turning point is not so sharp and varies according to the dye concentration. Some examples are shown in Fig. 1.

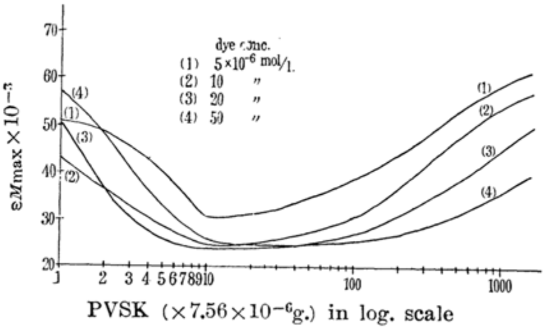

Fig. 1.—Change of molar extinction coefficient of M-band max. by P.V.S.K.

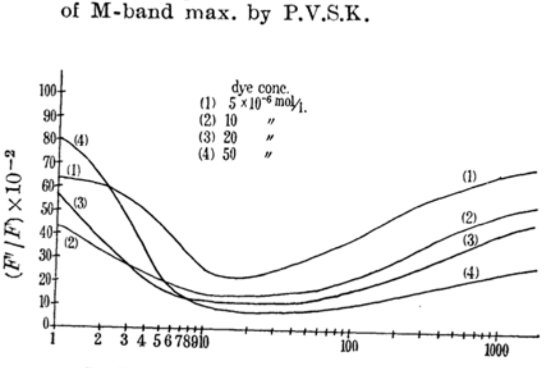

Fig. 2.—Change of relative fluorescence intensity (F'/F) by P.V.S.K.

Such behaviour is always observed in any concentration of dye between 5×10^{-6} mol./l. and 5×10^{-5} mol./l. In addition, it is to be noted that the position of M-Band does not change at all by the addition of PVSK and D-Band shows only a very feeble shift toward the shorter wave length.

(d) With the addition of PVSK the intensity of fluorescence decreases gradually at first until the concentration reaches the same critical value as the absorption, and beyond the critical concentration, the intensity gradually recovers with the further addition of PVSK. Some examples are shown in Fig. 2.

Discussion

As for the absorption spectrum of the aqueous Rhodamine 6 G solution, Levshin⁽⁴⁾ performed a quantitative study and analysed the result on the assumption that the spectral change with concentration depends upon the monomer-dimer ratio determined by the mass action law. He also measured the intensity of fluorescence and could roughly account for the concentration quenching as a result of the dimerisation on the assumption that only monomer can fluoresce while dimer cannot.

Our results for the aqueous dye solution (with no PVSK added) are quite in accord with his.

Now when PVSK is added, such behaviour as mentioned above (cf. c and d) is observed and these results can be explained very well by the following model.

" When PVSK is added to the aqueous solution of dye, the dye ion concentrates in the neighborhood of PVSK molecule (or it may conventionally be stated, that the dye ion is adsorbed on PVSK), where the association equilibrium shifts greatly toward the dimer; but the optical properties for both monomer and dimer such as electronic states related to the light absorption, absorption coefficient and efficiency of fluorescence are supposed to be influenced scarcely at all by this adsorption ". According to this model, it goes without saying that we can explain the observed decreases both in M-Band and in fluorescence intensity when a small quantity of PVSK is added; while the phenomena of recovery both in M-Band and in fluorescence when enough PVSK is added can be interpreted as follows.

When the added quantity of PVSK reaches a certain value (which depends on the concentration of dye), the dye concentration on the surface of PVSK will begin to decrease since the amount of dye in the whole system remains constant; then the association equilibrium will become shifted back again toward the monomer and the concentration of the monomer in the whole system increases, which causes M-Band and the fluorescence intensity to recover.

Thus Rhodamine 6 G-PVSK system seems to belong to the ideal case (2) described in the introduction.

Though the above qualitative explanation is very reasonable, there might be some other ways of explanation. For example, if the interaction between PVSK molecules, in the region of high concentration, becomes so great as to change their aggregation in some way, this change of aggregation in PVSK might cause the adsorbed dye molecule to be detached back into the solution as monomer.

In connection with such a possibility the recent report of Lovelock(5) is to be noted. He studied the fluorescence in almost the same system as ours and observed the same phenomenon of recovery; he did not however explain it clearly and attributed it rather ambiguously to the ionic effect. He seems to be of the opinion that the dye ion when attached to the high polymer loses its tendency for fluorescence. If this be true, the phenomenon of recovery must be exclusively due to the detachment of the dye ion, which will take place only when some remarkable change in the state of aggregation occurs in PVSK. This is very improbable in the case of PVSK, but, in order to confirm this more definitely, we have further examined our model more quantitatively in two ways as follows.

(1) First, on the assumption that the present system is the ideal case (2) the molar fraction of the monomeric ion in the whole system can be calculated from the following two equations ((1) and (2) respectively refer to the absorption data and fluorescence data).

$$x_M(A) = (2\varepsilon - \varepsilon_D)/(2\varepsilon_M - \varepsilon_D), \qquad (1),$$

$$x_M(F) = \frac{(F/c)(F'/F)}{(F/c)_{c\to 0}}. \qquad (2).$$

In equation (1), ε is the molar extinction coefficient at the peak of M-Band in any system, ε_M and ε_D are respectively that of monomer and dimer at the same position, which can be obtained when the concentration of dye is extrapolated to zero or infinite.

In equation (2), F is the intensity of fluorescence when the dye concentration is c and no PVSK is added, while F' is the same quantity when some PVSK is added at the same concentration of dye. The values of F'/F and $(F/c)/(F/c)_{c\to 0}$ can be obtained from the experiment and $x_M(F)$ can thus be calculated.

We have calculated $x_M(A)$ and $x_M(F)$ in the whole range of concentrations of dye and PVSK. The results can be summarised as follows.

When the concentration of dye is 5×10^{-6}mol./l., $x_M(A)$ and $x_M(F)$ coincide almost completely in the range from 7.56×10^{-6} g. to $2000\times7.56\times10^{-6}$ g. of the added PVSK, as shown in Table 1. As the dye oonconcentration is increased, the ratio $x_M(\mathrm{A})/x_M(F)$ gradually increases to some extent*; the result suggests the existence of some other effects of the high polymer on fluorescence, which are not taken account of in our model. In spite of such a discrepancy, the values of $x_M(A)$ and $x_M(F)$ change almost in parallel over a wide range of concentrations both of the dye and PVSK.

Table 1

$x_M(A)$ and $x_M(F)$ for various quantities of added PVSK.

dye conc. (mol./l.)	conc. of PVSK (unit $=7.56\times10^{-6}$g.)	$x_M(A)$	$x_M(F)$
5×10^{-6}	0	0.95	0.87
	1	0.56	0.55
	2	0.52	0.46
	4	0.44	0.47
	10	0.24	0.21
	25	0.26	0.21
	125	0.39	0.36
	200	0.48	0.44
	1000	0.68	0.58
	1500	0.76	0.77
	2000	0.79	0.56
10×10^{-6}	0	0.94	0.79
	1	0.44	0.34
	2	0.34	0.26
	10	0.22	0.11
	25	0.17	0.12
	125	0.27	0.17
	250	0.39	0.26
	500	0.44	0.37
	1000	0.61	0.39
	1500	0.62	0.54
	2000	0.70	0.46

Those results including Table 1 are considered to support our model quite well.

(2) Next, we have tried, on the basis of our model, to derive a theoretical relation between $x_M(A)$ on one side and the change of concentrations both of dye and PVSK on the other, in order to examine more precisely whether the experimental results can be reconciled with the model.

For this purpose, we have further assumed such a simple model of adsorption as the following; the adsorption equilibria are supposed to be established separately for monomer and dimer according to the following two equations.

$$C_M' = k_M C_M, \qquad (3),$$

$$C_D' = k_D C_D. \qquad (4).$$

where C_M and C_D are, respectively, the concentrations of monomer and dimer in the solution (in mol./l.) while C_M' and C_D' are the concentrations of the two species on the surface of the adsorbent (i.e. PVSK) (in mol./cm^2.).

In addition to these two equations, the mass action law obviously holds in the solution

$$C_M^2/C_D = \boldsymbol{K}, \qquad (5),$$

We put further

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(5) J. E. Lovelock, *J. Chem. Soc.* **1951**, 115-20.

* Levshin (4) has observed such a discrepancy even in the simple aqueous solution of Rhodamine 6 G.

P : number of grams of PVSK
S : the area of adsorbent per 1 g. (in cm.^{2})
V : the volume of solution (in cm.^{3})
C_0: the analytical concentration of the dye (in mol./l.)

then, starting from the above three equations (3) (4) (5) we can easily derive the following equation

$$\frac{y^2}{ZK}=\frac{(1+a_M P)^2}{1+a_D P}, \tag{6}$$

where y and Z are concentrations of the monomer and dimer, respectively, in the whole system which are given by equations (7) and (8)

$$y=\frac{C_M(V+k_M SP)}{V}, \tag{7}$$

$$Z=\frac{C_0-y}{2}, \tag{8}$$

a_M and a_D are the quantities given as follows

$$a_M=k_M S/V$$
$$a_D=k_D S/V.$$

It is remarkable that the equation (6) has the peculiar character that y^2/ZK is a universal function of the quantity of added PVSK alone, irrespective of the dye concentration. If this relation really holds between the experimentally obtained y^2/ZK values and P, we may conclude the correctness of our model with much confidence.

Now the value of y can be calculated from the relation $y=c_0 x_M(A)$* with the use of the experimentally obtained $x_M(A)$ value, and Z-value is also easily calculated by the relation (8). Thus, we have tested the applicability of the relation (6) for the experimental data. It turned out that they obey the relation (6) quite well throughout the whole range of experiment covering from 5×10^{-6} mol./l. to 5×10^{-5} mol./l. for dye concentration and from 7.56×10^{-6} g. to 15.17×10^{-3} g. for PVSK. Especially, when P is large, the theoretical requirement is satisfied almost quantitatively; in this region, the equation (6) is put approximately as follows,

$$\frac{y^2}{ZK}\approx\frac{a_M{}^2}{a_D}P+2\frac{a_M}{a_D}, \tag{9}$$

and the single universal linear relation must hold between y^2/ZK and P irrespective of the dye concentration. The experimental data have proved to satisfy this condition almost completely as shown in Fig. 3.**

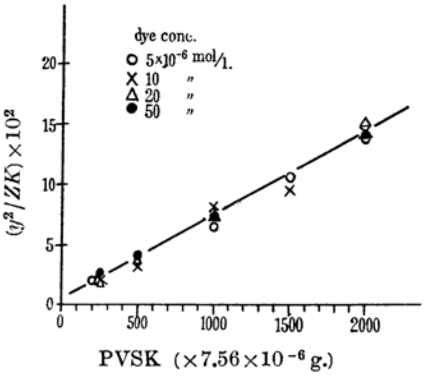

Fig. 3.—$(y^2/ZK)\sim$P diagram for various dye concentrations.

In the opposite extreme case where the quantity of PVSK is small, (6) becomes approximately as follows

$$\frac{y^2}{ZK}\approx\frac{1}{1+a_D P} \tag{10}$$

In this region, the situation is not so good; at the fixed P-value, the experimental y^2/ZK values for the different dye concentrations differ a little from one another, though, for each dye concentration, the variation of the value y^2/ZK against P conforms with the above relation. This disagreement may, however, be attributed to the inadequacy of the equations (3) and (4) in this region. For, when the dye concentration is moderate and the quantity of PVSK is very small, the adsorption is more or less in the neighbourhood of saturation, and it may be a better approximation to put

$$C_M'=0,\quad C_D'=\text{const}$$

instead of (3) and (4). Then the equation (10) becomes

$$\frac{y^2}{ZK}=\frac{1}{1+\frac{C_D' SP}{C_D V}}, \tag{11}$$

which agrees with the experimental results at least qualitatively. With (9) and (10) or (9) and (11), we can estimate the value of a_M and a_D as follows

$$a_M\simeq1.6\times10^3$$
$$a_D\simeq1.3\times10^5.$$

Therefore

$$k_M/k_D=1/100.$$

Thus we can conclude, on the basis of the ideal case (2), that when the dimer ion is adsorbed on PVSK about 100 times more than the monomer, the change of absorption spectrum such as experimentally observed can be explained almost quantitatively.

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* For some reasons x_M (A) is more reliable than x_M (F).

** Thus, in this region are approved not only our proposition that the present system of metachromasy is the ideal case (2), but also the simplified model of adsorption (equation (3) and (4)).

Conclusion

Two ideal cases for metachromasy were proposed: (1) one in which the effect is simply due to the change of the electronic state in the dye ion as a result of the interaction between the dye ion and metachromatic molecule, (2) the other in which the effect is simply due to the change of aggregation caused by the adsorption of the dye ion on the metachromatic substance. Two such effects are considered to be superposed in a general case. Rhodamine 6G-PVSK system can be explained almost quantitatively as a second ideal case.

The full account of the experimental data and the extensive discussion including other experimental results will be published in J. Inst. Polytech. Osaka City University.

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