Influence of the Addition of High Molecular Electrolyte upon the Absorption Spectra and Fluorescence of Organic Dyestuffs. III.

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Introduction

In the first paper[1] of the series of investigation about "the influence of the addition of high molecular electrolyte upon the adsorption spectrum and intensity of fluorescence of dyestuffs", it was stated at first that two kinds of mechanisms for metachromasy are to be taken into account in order to treat the problem from a general standpoint.

One is a) the change of electronic state of dye ions, directly produced by their interaction with high molecular electrolyte, and the other is b) the change in the state of aggregation of dye ions, which is caused by the accumulation of dye ions in the neighbourhood of high molecular electrolyte. In that paper, we succeeded in interpreting quantitatively the behaviour of Rhodmaine 6G–PVSK system, in which no metachromatic band appears, upon the basis of monomer-dimer equilibrium. In Part II we gave strong evidence that the spectral behaviour of Pyronine G–PVSK system, in which a metachromatic band appears, can also be explained only by the change of aggregation of dye.

Hitherto we have intentionally chosen such systems in which the change of aggregation is expected to be important, and the above two examples are the ideal case of b) which are interpreted quantitatively. Among various dyes so far investigated, there are many which can be comprehended along the same line, though not so quantitatively and accordingly not so definitely as the above two examples.

Now, turning our attention to the other case, we have chosen various Na and K–alkyl sulfate esters of different chain length as the electrolyte with only one functional group, and studied their influences upon the absorption spectra and fluorescence intensities of many dyes, in order to find out such a system as can be interpreted as an ideal case a).

As a result of a systematic study of many dyes, it has been confirmed quite definitely that in such cases the change of aggregation of dye ions still plays an important role. In addition, we have obtained some evidences which suggest that prior to micell-formation (at which a remarkable change of absorption spectrum and fluorescence intensity occurs,

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

[1] M. Koizumi and N. Mataga, This Bulletin **26**, 115 (1953), See also: N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **3**, 21 (1952).

as is observed usually in other cases[2]) the high molecular electolyte lies in some aggregated state or in an orderly array of some kind. By virtue of it, the dye ions also take such a special state of aggregation as produce a peculiar type of change in absorption spectra and intensity of fluorescence.

In this paper some experimental results which support the above viewpoint, especially those about Rhodamine 6G, will be reported in a rather condensed form, the details of which will be published in Journ. Inst. Polytech. Osaka City University.

The chief points which we have investigated are 1) the effect of chain length of alkyl sulfate, 2) the effect of the dye concentration and 3) the effect of temperature.

The discussion will be given not separately but along with the experimental results in each part.

Experimental Results and Interpretation of Them

(1) The Effect of Chain Length of Alcohol Sulfate Ester—Methyl and butyl sulfate do not affect the spectrum nor the fluorescence at all, irrespective of the magnitude of addition. Amyl sulfate gives a slight effect only at its high concentrations. In the case of octyl sulfate, the quenching of fluorescence is observed accompanied by the complicated change of absorption in the region above 5×10^{-4} mol./l. When the concentration reaches C. M. C., the fluorescence recovers and the spectrum becomes simple again similar to that of pure aqueous solution.

Na-lauryl sulfate (LASNa) shows an analogous effect as octyl sulfate except that the effect becomes observable at a little lower concentration, ca. 10^{-5} mol./l. Analogous phenomena are also observed in some dyestuffs other than Rhodamine 6G such as Trypaflavine and Acrydine yellow, which have a tendency to polymerize in the pure aqueous solutions [1,3]) while Rhodamine B, which does not dimerize in the aqueous solution[1]) suffers no effect, however much LASNa is added. All these results strongly support the view that only in the case when such electrolytes as can form the micelle are added to dimerizable dyestuffs, the fluorescence is quenched and the absorption changes prior to C. M. C.

(2) The Effect of the Concentration of the Dye.—When the dye concentration is small (2×10^{-6} mol./l.), the effect comes to be observed at higher concentration of LASNa while the recovery of fluorescence begins at a far lower concentration than C. M. C. reported in the literatures[4]), which was determined, for example, from the measurement of electric conductivity. As regards the absorption spectrum, α-band declines and β-band slightly rises in the region where the quenching of fluorescence is remarkable. The above results can be comprehended if the dye ions in the proper concentration of added LASNa are assumed to exist as something like dimer sandwiched in between the ions of added electrolytes, and have no power of fluorescence. The interpretation is quite analogous to the case of PVSK. Thus when the concentration of dye is low, the gradual increase of LASNa soon comes to provide, prior to C. M. C., such a situation in which the dye ions in the neighbourhood of the aggregate of LASNa begins to decrease, and this causes the above phenomenon of recovery.

On the other hand, when the concentration of dye is large, the quenching is observed in a wider range of concentration of LASNa, and the magnitude of quenching is more remarkable than in the case of lower concentration of dye. Quenching is removed sharply in the close neighbourhood of C. M. C. of LASNa. As for the absorption spectra, both α-and β-band decline at first, with the addition of LASNa; then a broad band appears extending to the longer wave length than α-maximum, which in the suitable concentration of LASNa has two peaks in the opposite side of the position of α-band. Thus the spectrum is quite different from that of simple or PVSK added[1]) aqueous solution, and this result may reasonably be comprehended if one assumes that dye ions are sandwiched in between the orderly array of electrolyte, and interaction between these dye ions are such that the situation is somewhat analogous to but different from that of dimerization or polymerization in the aqueous solution. It goes without saying that the quenching is also interpreted on the basis of the same model. It may be added that in the case of high concentration of dye, the number of sandwiched dye ions between the orderly array of electrolyte ions would be so large that it could not be decreased so much, prior to C. M. C., and this may be the reason why the recovery takes place at C. M. C. without any sign of it beforehand. The similar changes in absorption spectrum and intensity of fluorescence are also observed in the case of other dyes which

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[2]) See for example; M. L. Corrins and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947); *J. Chem. Phys.*, **14** 641 (1946), R. C. Merrill and R. Getty, *J. Phys. Colloid Chem.*, **52**, 774 (1948).

[3]) V. Zanker, *Z. Phys. Chem.*, **199**, 225 (1952).

[4]) See for example; F. D. Haffner, G. A. Piccione and C. Rosenblum, *J. Phys. Chem.*, **46**, 662 (1942).

have some tendency of polymerization such as Trypaflavine and Acridine yellow[1,3] and they are also considered to be due to the same circumstances. On the other hand, Pyronine G which sustains no effect by PVSK in the small concentration of dye (Part II), also shows no change in either absorption spectrum or fluorescence in the present case, as long as the concentration of dye is low. As for Rhodamine B which has no tendency of polymerization, the result was already mentioned in section 1.

The difference of spectrum in the case of LASNa from that with PVSK seems to exist generally. Thus Pyronine G, in a very limited region of dye concentration, shows a similar metachromatic band as in the case of PVSK, but elswhere, it commonly gives a broad band different from that of the aqueous solution. Other dyestuffs such as Thionine and Toluidine blue etc., show similar behaviour. The problem would be worthy of further study with regards to the change of electronic state of dye ion influenced by the ions of electrolyte.

Judging from the above results, it may be safe to conclude that the change of spectrum and fluorescence in the case of LASNa is essentially related to the change in aggregation of dye ions just as in the case of PVSK.

(3) **The Effect of Temperature.**—The intensities of fluorescence were measured at 13° C. and at 55°C. in various corresponding conditions and were compared with each other. It was found that as long as the concentration of dye is small (2×10^{-6} mol./l.), the intensity is reduced by the elevation of temperature when the quantity of added LASNa is small (up to 2×10^{-4} mol./l.); while at higher concentration of LASNa the intensity is stronger at a higher temperature. Now, as for the effect of temperature, two phenomena must in general be taken into account. One is the collisional quenching[5], which increases at higher temperature, and the other is the shift of association equilibrium between dye ions or between electrolyte and dye ion, which generally tends toward dissociation at higher temperature. If it is assumed that the above two effects are operative in the present system, then the results can at least qualitatively be well interpreted. Thus the collisional quenching naturally predominates at low concentration of LASNa where the aggregates of LASNa are not existent in measurable quantity, and the result is that the intensity is reduced at higher temperature. While at higher concentration of LASNa, a relatively large portion of dye ions are sandwhiched in between the orderly array of LASNa ions, and the shift of association equilibrium determines the resultant temperature effect. According to the above interpretation, the temperature effect ought to be, in general, positive at higher concentration of dye, and the experimental result is just as expected.

It may further be added that the features of absorption spectrum becomes relatively simpler at higher temperature, which is also reconciled with the above interpretation. Thus the temperature effect can also be comprehended if one assumes that the dye ions sandwiched in between the orderly array of electrolyte ions, interact with each other in a somewhat similar manner as in the bulk solution.

General Conclusion

From the above-mentioned experimental results and discussions, it has become quite clear that the change of absorption spectra brought about by the addition of an electrolyte with only one functional group, is essentially correlated with the change of aggregation of dye ions. But, in contrast to such substances with many functional groups as PVSK, it seems indispensable that some kind of specific aggregation or orderly array of ions exists on the part of added electrolyte. The structure of it is naturally considered to be quite labile, and accordingly the aggregation of dye ions, an orderly array of electrolyte ions and the interaction between dye and electrolyte ions, all these phenomena, are entangled with each other in so delicate a manner that the spectrum is expected to be influenced by various factors very sensitively as is the case.

This problem would be very interesting from the standpoint of the change of electronic state of dye affected by the neighbouring electrolyte ion, that is from the standpoint of case (a) mentioned at the beginning of the present paper.

To sum up our results reported in three papers, it can be concluded that in the case of basic dyes such as Xanthene or Thiazine dyestuffs, metachromasy produced by the addition of anionic electrolyte is chiefly caused by the change of aggregation of dye ions (mechanism b) though the change of electronic state of dye directly produced by the interaction between dye and electrolyte ions (mechanism a) may be superposed in some cases. Our general conclusion is quite similar to that of Michaelis[6], but our reasoning is more

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[5] See for example: P. Pringsheim, "Fluorescence and Phosphorescence", 322. 349 (1949).

[6] L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**. 1212 (1945), L. Michaelis, *J. Phys. Colloid Chem.*, **54**, 1 (1950).

definite being supported by some quantitative discussions.

More detailed discussions involving other dyestuffs will be reported in Journ. Inst. Polytech. Osaka City University. The cost of this reseach has been partly defrayed from the Scientific Grant from the Ministry of Education.

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