

Measurement and Analysis of Adsorbed Amount of a Sensitizing Dye on Each AgBr Grain by Microscope Spectroscopy

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Abstract

The absorption spectrum of a dye adsorbed on a single silver halide emulsion grain was measured by means of a microscope spectrum photometer and the amount of the dyes adsorbed on each grain was evaluated by its absorption intensity. It was revealed that the uniformity of the amount of the adsorbed dyes among grains was reduced by the growth of J aggregates, and that the concentration of the free dye needed for the nucleation of J-aggregates was higher than that for the growth. It is considered that the nucleation and growth model, as was applied to the formation of silver halide grains, also holds for the formation of J-aggregates.

Introduction

J-aggregates of cyanine dyes are very important for spectral sensitization of silver halide photographic materials because of their sharp and intensive absorption band (i.e.J-band). Many studies on dye adsorption and J-aggregation have ever been reported. Especially attempts to directly observe J-aggregates on each grain are very important, because they give such direct information as the adsorption sites, size, structure, and formation process of J-aggregates.

Maskasky[1)] observed luminescence images of very large J aggregates of various cyanine dyes by means of a low temperature luminescence microscope and determined the epitaxial orientation of dye molecules forming their J-aggregates.

Saijo et al[2)] also observed cathode luminescence image of J aggregates by means of an analytical color fluorescence electron microscope, and referred to the distribution of the amount of adsorbed dyes among grains.

An atomic force microscope, a scanning electron microscope, a nearfield optical microscope ,and others have been also used to characterize J-aggregates of cyanine dyes on silver halide emulsion grains.

In this paper, we used a microscope spectrum photometer and measured for the first time an absorption spectrum of J aggregates of a dye on a single silver halide tabular grain.

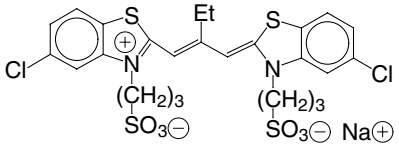
An integral of an optical density versus wave number of the spectrum corresponds to the product of the concentration and oscillator strength of the dye. And it was possible to estimate to the amount of the adsorbed dye on each grain, because the oscillator strength was considered to be invariant regardless of their aggregates formation.

The distribution of the amount of the adsorbed dye among grains was obtained by applying the above procedure to several tens grains. We now report a new concept of adsorption of cyanine dyes to silver halide grains and their J-aggregation by analyzing the distribution of the amount of the adsorbed dye among grains and comparing it with the simulated random distribution.

Experimental

The emulsion used in this study consisted of tabular silver bromide grains having main surfaces with average diameter of 2.4μm.

The dye used in this study was 3,3'-bis-(3-sulfopropyl)-5,5'-dichloro-9-ethyl-thiacarbocyanine (Dye 1).



Dye1

A microscope spectrum photometer (MSP65, Carl Zeiss) was used to measure an absorption spectrum of a single silver bromide grain. Absorption intensity was defined in this study as the product of absorbance and half width of a spectrum. Absorption intensity corresponds to the product of the amount of the adsorbed dye and their oscillator strength.

Results and Discussion

Figure 1 shows an absorption spectrum of a single grain with J-aggregate of Dye 1 adsorbed (the surface coverage of the grains by Dye1 was 60%). The spectrum had its absorption maximum at the same wavelength as that of the bulk emulsion, and did not change on repeated measurements.

Figure 2 shows that the absorption intensity averaged over 25 grains was proportional to the surface coverage of the grains by Dye 1, and the adsorbed amount of Dye 1, and that the absorption intensity of several tens grains gave the distribution of the amount of adsorbed dye among the grains.

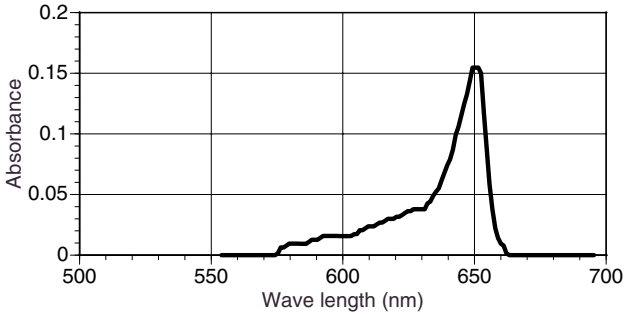


Figure 1 . Absorption spectrum of J-aggregates of Dye 1 on a single AgBr tabular grain.

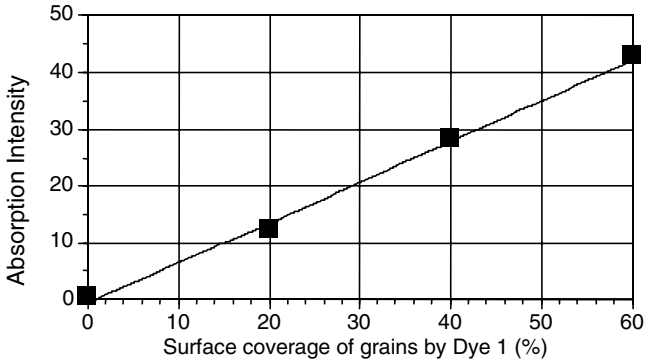


Figure 2 . Relation between surface coverage of grains by Dye 1 and absorption intensity.

Figure 3 shows the distribution of the amount of the adsorbed dye among grains when the average surface coverage of the grains by Dye 1 was 60%.

The observed distribution was compared with the rondom distribution in the absence of any intermolecular interaction on the basis of the hypergeometric distribution model. The coefficient of variation of hypergeometric distribution is represented by following equation.

$$\sqrt{\frac{(1-1/n)(1-a/mn)}{(1-1/mn)a/n}}$$

where n is the number of grains in the emulsion , m is the number of dye-adsorbing sites a grain, and a is the number of added dye molecules.

As shown in Figure 4, the coefficient of variation calculated for the random distribution was 0.024%, while the observed one was 19.7%. It was therefore revealed that the observed distribution was very polydispersed.

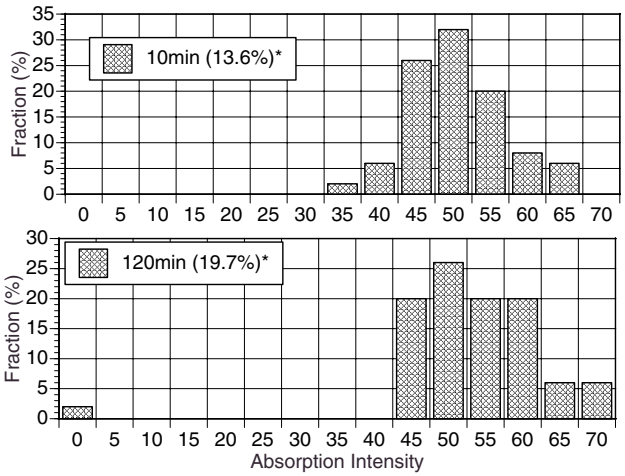


Figure 3 . Change in the distribution of amount of adsorbed Dye 1 among the emulsion grains at 10min. (above) and 120min. (below) after Dye1 addition.
**coefficient of variation*

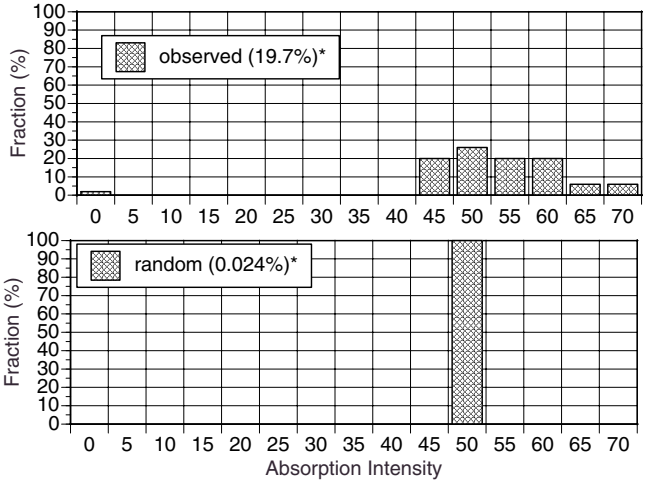


Figure 4. Comparison between the observed and rondom distribution of amount of adsorbed Dye1 among the emulsion grains.
**coefficient of variation*

An important reason for the polydispersed distribution was the reduction of freedom of dye molecules due to the growth of J-aggregates.

Figure 5 shows the distribution of the adsorbed amount of Dye1 among grains after slowly introducing the

additional dye to the mixture of dyed and undyed emulsions at high temperature.

In spite of the introduction of the additional dye, most undyed grains remained undyed. This result indicated that the additional dye was preferably adsorbed to the dyed grains, and it can be explained on the basis of the potential energy profile of Dye 1 molecules in small and large aggregates, as shown in Figure 6[3]. Namely, dye molecule in a large J-aggregate is more stable than that in a small one. Therefore, the additional dye molecules were likely to be adsorbed to grains with large J-aggregates rather than to undyed grains and grains with small J-aggregates.

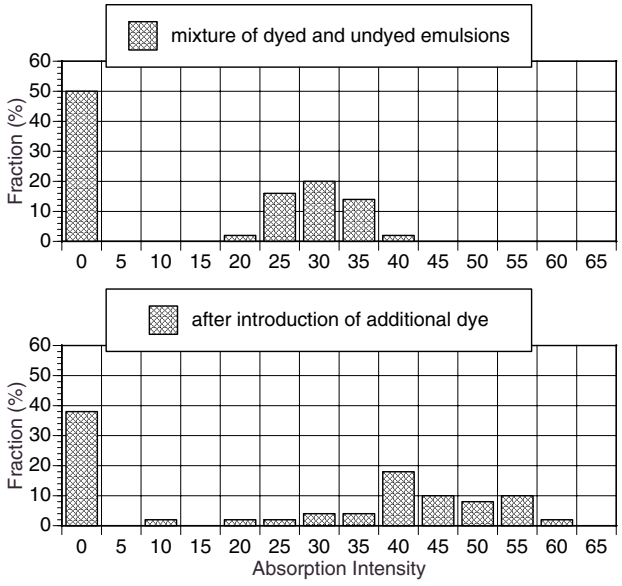


Figure 5 . The distribution of the adsorbed amount of Dye 1 among grains after introduction of additional dye to the mixture of dyed and undyed emulsions (slow addition at high temperature).

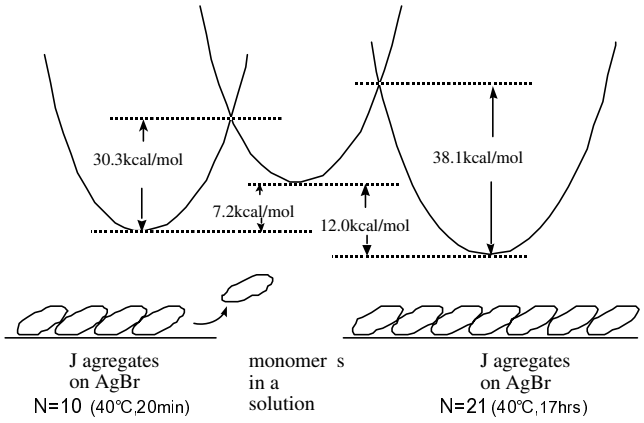


Figure 6 . Potential energy profile of Dye 1 molecules in small and large aggregates (the numbers of the molecules were 10 and 21/aggregate, respectively) on AgBr and in a solution as monomers.

The J-aggregation as described above could be explained on the basis of the nucleation and growth model, as applied to the formation of silver halide grains. There are two characteristic concentrations of solutes or free dye molecules; C1 is the concentration in equilibrium with the grains or J-aggregates and the minimum concentration for their growth and C2 is the minimum concentration for the nucleation of the grains or J-aggregates, as shown in Figure 7.

According to Figure 7, the nucleation of J aggregates was supposed to be influenced by the rate of dye addition and the rate of the growth of J aggregation. It is known that the rate of the growth of J-aggregation increased with increasing temperature[3,4].

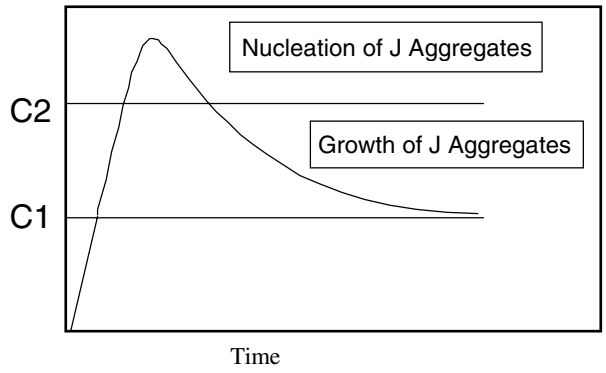


Figure 7. Change in dye concentration con the basis of the nucleation and growth model of J-aggregates.
C2(the minimum dye concentration for nucleation) >C1(that for growth)

Figure 8 shows the distribution profiles of the adsorbed amount of Dye 1 among grains, which were achieved under three different dye addition conditions, (a) slow addition at high temperature, (b) fast addition at high temperature, and (c) slow addition at low temperature of the dye, to the mixture of dyed and undyed emulsions. After the slow addition at high temperature (a), most undyed grains remained undyed, while after the fast addition at high temperature (b) and the slow addition at low temperature (c), the number of undyed grains decreased significantly. It was considered that the concentration of free dye was determined by the rate of its increase due to the dye addition and the rate of its decrease of due to the growth of J-aggregates, and was therefore more likely to exceed C2 under the conditions (b) and (c) than under the condition (a). This behavior was similar to that observed for silver halide grain formation process.

There was another analogy of the formation processes between silver halide grains and J-aggregates of dye from the viewpoint of Ostwald ripening, as shown in Figure 8. It is known that the size of J aggregates of Dye1 increased with increasing temperature.

Two emulsions, to which Dye 1 was added at different temperature, were mixed to give an emulsion containing the grains, which adsorbed J-aggregates with

different size. When the mixed emulsion was digested, the distribution of the adsorbed dye amount among grains became polydispersed as shown in Figure 9. It was considered that dye molecules moved from the grains with smaller J-aggregates to the grains with larger ones owing to the Ostwald ripening of J-aggregates.

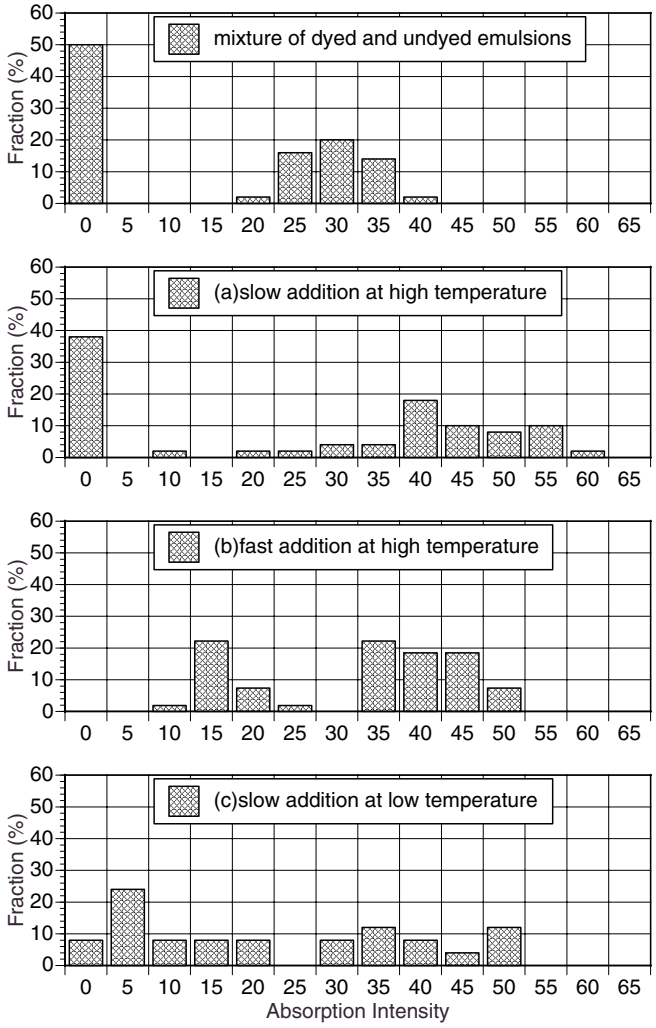


Figure 8 . The distribution of the adsorbed amount of Dye 1 among grains after (a)slow addition at high temperature ,(b)fast addition at high temperature ,(c)slow addition at low temperature ,of additional dye molecules to the mixture of dyed and undyed emulsions.

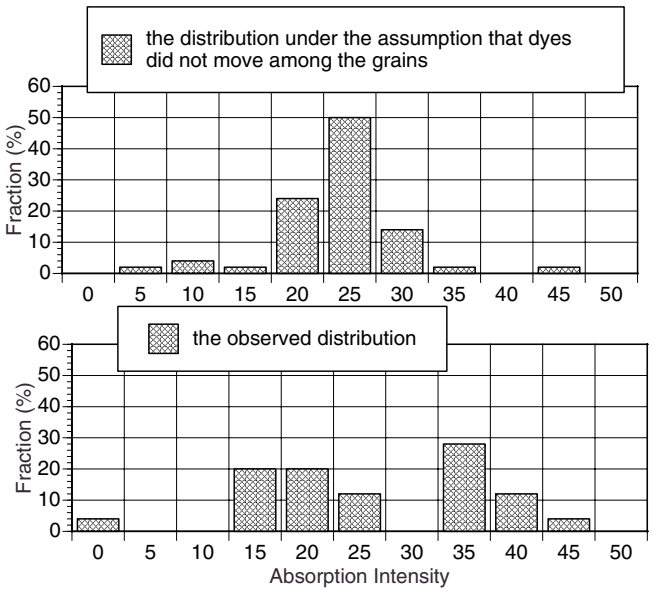


Figure 9. Ostwald ripening of J-aggregates of Dye 1
Comparison of the observed distribution with the distribution under the assumption that dyes did not move among the grains ,in the mixture of the two emulsions that Dye 1 was added at different temperature.

References

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Biography

Katsuhiro Yamashita received his M.S.degree in Chemistry from Kyoto University in 1992. Since 1992 he has been a member of Ashigara research laboratories, Fuji Photo Film Co. Ltd. His work has primarily focused on the spectral sensitization of silver halide emulsion.