Structure and Growth Mechanism of J-Aggregates of a Cyanine Dye Adsorbed on AgBr Grains from Thermodynamic Analysis of the Dye Desorption Process

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The structure and mechanism of J-aggregates of a sensitizing dye formed on AgBr grains in emulsions were investigated on the basis of thermodynamic analysis of the desorption process of dye molecules from the grains by use of a macroporous cross-linked polystyrene resin as an adsorbent for the dye. The desorption rate did not depend on the residual dye concentration on the grain surface, indicating that J-aggregates were linear (or two-dimensional) in structure. The increase in the average size of J-aggregates on the grains caused (1) the decrease in the desorption rate, (2) increase in the activation energy for the desorption, and (3) increase in the heat of adsorption ($-\Delta H$) of the dye to the grains. Thermodynamic analysis of these results supported the previously proposed mechanism, according to which J-aggregates of a dye on silver halide grains grew through the repetition of the desorption and adsorption of dye molecules on the grains.

1. Introduction

Many cyanine dyes are adsorbed on silver halide grains by forming J-aggregates which are characterized by their sharp absorption band with bathochromic shift of their absorption maximum (i.e., J-band).[1] Many efforts have been paid to the analysis of J-aggregates because of their scientific interest and practical importance for spectral sensitization in photography.[2−4] However, the mechanism of J-aggregate formation is still obscure due to lack of effective methods for the analysis of J-aggregates.

Tani successfully analyzed the desorption process of J-aggregates of a cyanine dye from {111} faces of silver halide grains and analyzed the growth mechanism of the J-aggregates by using a dye, which was preferentially adsorbed on {100} faces of the grains.[5] This method relied upon dyes such as 3,3′-bis(4-sulfobutyl)-9-methylthiacarbocyanine, which was preferentially adsorbed on the {100} face and provided a double band with absorption maxima at 520 and 600 nm and provided J-band at 630 nm on the {111} face. Tani demonstrated that the desorption process of the J-aggregated dye molecules on the {111} faces could be successfully monitored by following the change in the diffuse reflectance at 630 nm after an emulsion with undyed cubic grains was added to an emulsion with octahedral grains which adsorbed the J-aggregated dye molecules. Since the desorption rate did not depend on the residual dye concentration, obeying the zero-order reaction, Tani had concluded that J-aggregates of the dye were linear in structure on the octahedral grains, and the desorption occurred only at the terminal molecules of the aggregates. Although this method is effective in principle for the analysis of adsorption states and structure of J-aggregates on silver halide grains, it is applicable to only such a dye with adsorptivity and adsorption spectrum that are considerably different on {100} and {111} faces of silver halides.

In order to apply the above-stated method to J-aggregates of dyes other than 9-methylthiacarbocyanine dyes on silver halide
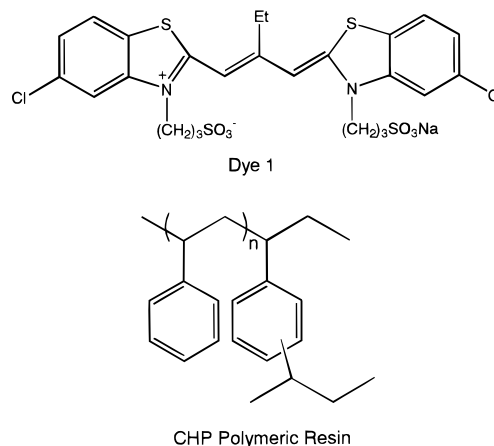
Figure 1. Molecular structures of the dye and porous cross-linked polystyrene resin (CHP) used in this paper.

grains, it is required to desorb J-aggregated dyes on silver halide grains by appropriate adsorbents which adsorb the dyes more strongly than silver halide grains. In the present paper, porous cross-linked polystyrene resin was found to be an appropriate adsorbent for the above-stated purpose. Adsorption−desorption behavior and structure of J-aggregates were also demonstrated from thermodynamic analysis of the dye desorption process by using the above-stated adsorbent.

2. Experimental Section

2.1. Materials. Figure 1 shows the molecular structures of the dye (dye 1) and cross-linked macroporous polystyrene resin CHP-20P (abbreviated as CHP hereafter) used in this paper. A mixture of methanol and water (1:1 in volume) was used as a solvent for a solution of dye 1 and as a medium for a suspension of CHP. Dye 1 was adsorbed on AgBr emulsion grains, forming J-aggregates. The resin CHP was commercially provided by Mitsubishi Chemical Corp. and was dried in vacuo after having been washed with methanol before use.

The emulsions used in this investigation were composed of 0.762 mol/dm^3 of octahedral and cubic AgBr grains in aqueous gelatin solution. The average edge lengths of the octahedral and cubic grains were 0.78 and 0.68 μm, respectively. They were prepared by the controlled double-jet method.[6]

2.2. Desorption of Dye Molecules from Emulsion Grains. A dyed emulsion was prepared by adding 2 mL of a dye solution (1 mmol/dm^3) to 25 g of an emulsion, which was then stirred (i.e., ripened) at fixed temperature and period. All the dye 1 molecules added to the emulsion were adsorbed on the AgBr grain, and the surface coverage of the grains with dye 1 was 20%.

A fixed amount of a suspension of CHP was added to a dyed emulsion, which was then stirred at fixed temperature and period. Dye molecules were desorbed from AgBr emulsion grains and adsorbed on CHP polymeric resin during the above-stated treatment. The diffuse reflectance spectrum was measured for an emulsion in a thick cell by use of a Hitachi 307 type color analyzer under the condition that the surface reflection of the cell was compensated. The amount of adsorbed dye molecules on AgBr emulsion grains was determined from the reflectance according to the following Kubelka−Munk equation.[7]

$$K/S = (1 - R_\infty)^2/2R_\infty = c\epsilon/S \tag{1}$$

where K and S are the absorption and scatter coefficients of the emulsion, respectively, c is the concentration of the dye in a specified state, ϵ is the extinction coefficient of the dye molecules, and R_∞ is the diffuse reflectance of the emulsion at the wavelength that is absorbed by the dye in the above-mentioned state.

2.3. Determination of Thermodynamic Parameters. The heat of adsorption ($-\Delta H$) of dye 1 to AgBr emulsion grains was measured with a twin calorimeter by adding 5 mL of a dye solution to 3 g of an emulsion at fixed temperature.

The free energy change (ΔG) for the adsorption of dye 1 to AgBr emulsion grains was determined from Eucken's method, which was based on the following equation:[8−10]

$$\Delta G = -2.303RT \log(10^4K/6.02\tau S_A) \tag{2}$$

where τ is the thickness of the adsorption layer and was taken as 7.7 Å according to the literature,[8] S_A is the area occupied by a single dye molecule on the grain surface, and K is the equilibrium constant for the adsorption of the dye. The value of K is given by Langmuir's adsorption isotherm as described below:

$$c/(\theta M) = c/M + 1/(KM) \tag{3}$$

where c is the concentration of free dye molecules (mol/dm^3); M and θ are the saturated amount of adsorbed dye molecules per unit surface area (mol/m^2) and surface coverage by adsorbed dye molecules, respectively.

The adsorption isotherm was obtained by adding 3 mL of a dye solution to 3 g of the above-stated AgBr emulsion at fixed conditions. The amount of adsorbed dye molecules on the emulsion grains (corresponding to θM in eq 3) was calculated from the value of c.

2.4. Size of J-Aggregates. The average number of dye molecules per J-aggregate was determined under the assumption that J-aggregates were linear in structure according to Knapp's equation, as shown below:[11]

$$\Delta\nu_{1/2}(M)/\Delta\nu_{1/2}(J) = N^{1/2} \tag{4}$$

TABLE 1: Average Size of J-Aggregates of Dye 1 Formed on AgBr Grains in Emulsions Which Were Ripened under Various Conditions

ripening condition		size of J-aggregates[a]	
temp, °C	time	octahedral grains	cubic grains
40	20 min	10	34
40	18 h	21	43
60	20 min	21	43
70	20 min	27	53

[a] The average number, N, of dye 1 molecules/J-aggregate, as estimated according to eq 4.
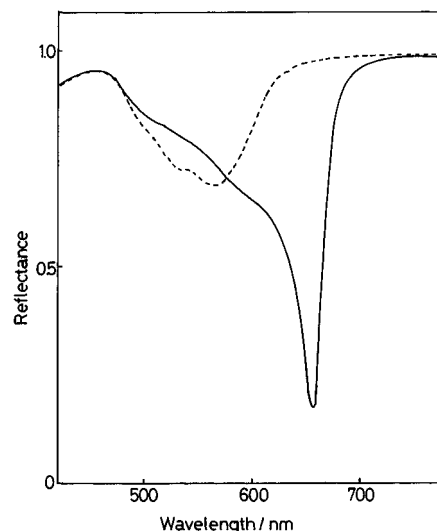
Figure 2. Diffuse reflectance spectra of octahedral AgBr emulsions with dye 1 in the absence (solid line) and presence (broken line) of CHP. J-aggregates of dye 1 were formed on the emulsion grains during ripening the emulsion for 20 min at 70 °C. The emulsion was then stirred for 18 h at 40 °C in the presence of CHP (1.5 g/25 g of emulsion).

where $\Delta\nu_{1/2}(M)$ and $\Delta\nu_{1/2}(J)$ denote half-line widths of absorption spectra of monomeric and J-aggregated molecules of a dye, respectively. The value of $\Delta\nu_{1/2}(M)$ was obtained from the absorption spectrum of monomeric molecules of a dye in its methanol solution. Table 1 summarizes the average size of J-aggregates of dye 1 formed on AgBr emulsion grains under various conditions.

3. Results and Discussion

3.1. Desorption of Dye Molecules in J-Aggregates from AgBr Grain Surface. Adsorption of dye molecules to AgBr emulsion grains was totally reversible since all the dye molecules were desorbed from the grains and adsorbed by CHP. The J-band with absorption peak at 655 nm, which was ascribed to dye 1 on octahedral AgBr emulsion grains, disappeared when CHP was added to the dyed emulsion as shown in Figure 2. The appearance of the absorption band with maximum at 563 nm, which was ascribed to the monomers of the dye, was in concert with the disappearance of the J-band, indicating that the dye molecules in J-aggregated state were desorbed from the grains and adsorbed to CHP in the monomeric state. The adsorption of the dye molecules on CHP could be also confirmed by the color of CHP, which was separated from the emulsion by filtration. Thus, the desorption process of the J-aggregated dye molecules could be monitored by measuring the diffuse reflectance of the emulsion at 655 nm corresponding to the J-band, since the dye molecules on CHP were monomeric and did not hinder the above-stated measurement. It was confirmed that changes in both pH and pAg of an emulsion caused by the

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addition of CHP was less than ±0.1. These facts clearly indicated that CHP was an excellent adsorbent for the investigation of desorption process of dye molecules from silver halide emulsion grains.

The polystyrene matrices of CHP have many hydrophobic pores. Thus, only molecules containing hydrophobic groups such as cyanine dyes were preferentially adsorbed on CHP with their hydrophilic groups, and inorganic ions remained in an emulsion phase. Consequently, dye molecules moved from emulsion grains, while pH and pAg were kept constant, when CHP was added to a dyed emulsion.

In a dyed emulsion with CHP added, dye molecules were desorbed from emulsion grains (process 1), diffused through the aqueous gelatin solution phase of the emulsion (process 2), and were adsorbed (process 3). Thus, process 1 should be investigated under the condition that its rate was independent of the rates of processes 2 and 3, both of which should depend on the amount of CHP added. Figure 3 showed the effect of the added amount of CHP on the desorption rate of dye 1 in J-aggregated state from octahedral AgBr grains. The rate of process 1 increased with increasing the added amount of CHP and was saturated with CHP of more than 8 g per 25 g of a dyed AgBr emulsion. The investigation of the desorption process was conducted with 10 g of CHP per 25 g of an emulsion.

3.2. Application of CHP to Analysis of Desorption Process of Dye Molecules from AgBr Emulsion Grains. Figure 4 shows the amount of residual dye 1 molecules in J-aggregated state on octahedral AgBr emulsion grains as a function of the time duration after CHP was added to dyed emulsions. The relative concentration of the residual dye molecules in an emulsion could be obtained by applying eq 1 to the diffuse reflectance of the emulsion at the wavelength corresponding to their J-band. As shown in Figure 4, the concentration of the residual dye molecules on the grains decreased linearly with the time duration, indicating that the desorption was the zero-order reaction as expressed by the following equations:

$$d([A_0] - [A])/dt = k$$

$$[A_0] - [A] = kt \qquad (5)$$

where $[A_0]$ and $[A]$ are the concentration of the dye on the grains (μmol/mol of AgBr) at $t = 0$ and t, respectively. The extent of the region (R) in which the desorption process obeyed the zero-order reaction was independent of desorption temperature. Similar zero-order desorption was also observed with other J-aggregated dyes on AgBr emulsion grains. The results of further investigation on dye 1 in J-aggregated state are shown in Figures 5 and 6. As seen in these figures, R increased, the desorption rate of dye 1 decreased, and the activation energy of the desorption rate increased with increasing the average size of J-aggregates.

3.3. Change in Thermodynamic Parameters with Increasing Size of J-Aggregates. The free energy change (ΔG) for the adsorption of dye 1 to AgBr grains could be determined from the adsorption equilibrium constant K, which was given by the intercept of the straight line in the Langmuir plot on the basis of eq 3, as shown in Figures 7 and 8. The areas occupied by a molecule of dye 1 (S_A in eq 2) on octahedral and cubic AgBr grains were determined as 81 and 74 $Å^2$, respectively, from the saturated amount of adsorbed dye 1 molecules M, which was given by the slope of the straight line in the Langmuir plot. The heat of the adsorption of mole of dye 1 to AgBr emulsion grains was independent of the surface coverage of the grains by the dye. The obtained values of the changes in
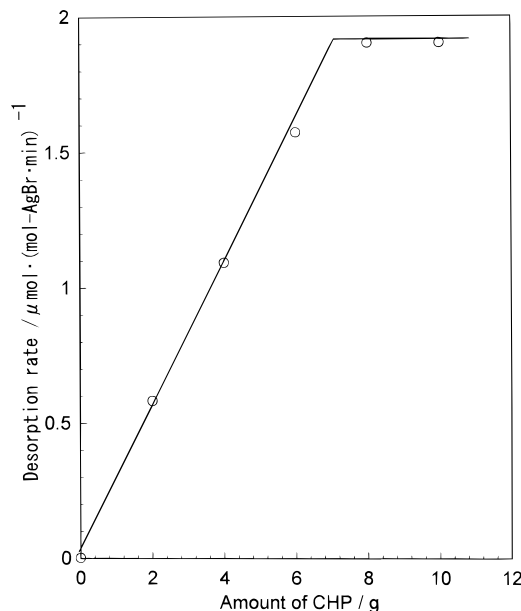

Figure 3. Effect of added amount of CHP on the desorption rate of dye 1 in J-aggregated state from octahedral AgBr emulsion grains.
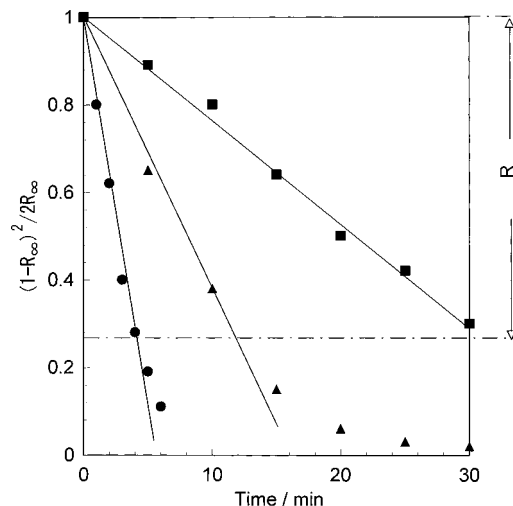

Figure 4. Amounts of dye 1 adsorbed on cubic AgBr emulsion grains as functions of time duration after CHP was added to dyed emulsions, which were ripened at 40.5, (●), 45.4, (▲), and 50.3 °C (■) in the presence of CHP. J-aggregates of dye 1 had been formed on the grains by ripening an emulsion with dye 1 for 20 min at 70 °C. The ordinate was normalized at $t = 0$. Within the region denoted by R, the desorption of dye molecules from the emulsion grains obeyed the zero-order kinetics as described by eq 5.

thermodynamic parameters for the adsorption of dye 1 to AgBr grains were summarized in Table 2. It could be concluded that larger J-aggregates were more stable than smaller ones on AgBr emulsion grains, as judged from the changes both in free energy (ΔG) and in heat of adsorption (ΔH) for adsorption of dye 1 to the grains.

3.4. Structure and Growth Mechanism of J-Aggregates. The fact that the desorption of dye 1 molecules in the J-aggregated state from AgBr emulsion grains occurred according to the zero-order reaction, as expressed by eq 5, indicates that the number of the adsorbed dye molecules that were ready for desorption remained constant during the zero-order desorption process. This result coincides with our previous conclusion,[5] suggesting that the fundamental structure of J-aggregates was linear (or two-dimensional) and the desorption occurred at the terminal molecules of J-aggregates. It is considered that
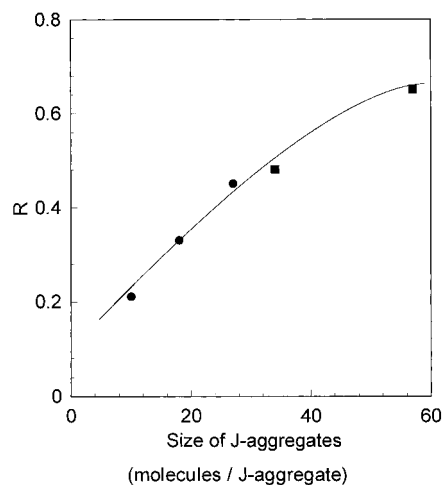
Figure 5. Dependence of the extent of the zero-order desorption region on the average size of J-aggregates of dye 1 formed on octahedral (●) and cubic AgBr grains (■).
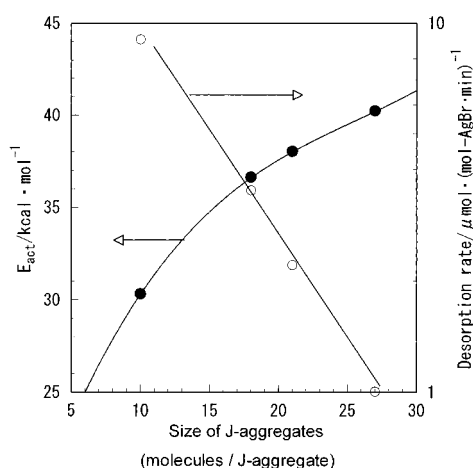

Figure 6. Rate and activation energy (E_{act}) of desorption of dye 1 molecules from octahedral AgBr emulsion grains as functions of the average size of J-aggregates of the dye on the grains.
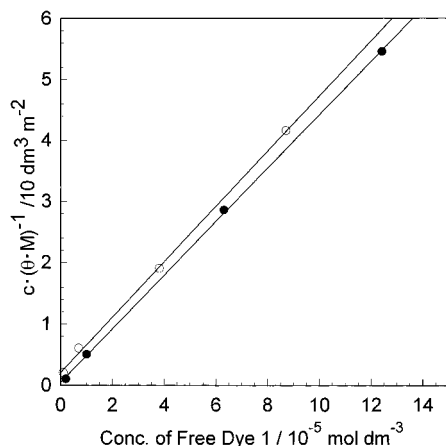

Figure 7. Langmuir plots on the basis of eq 3 for the adsorption of dye 1 to octahedral AgBr grains at 40 (○) and 60 °C (●).

the extent of the R as shown in Figure 4 corresponded to the maximum amount of dye molecules that could be desorbed without decreasing the number of J-aggregates present in the emulsion studied. Good correlation between the extent of the region R and the size of J-aggregates in Figure 5 supports the above-stated consideration. The measurement of the region R is expected to provide one of the methods to get the knowledge of the size of J-aggregates on silver halide emulsion grains.
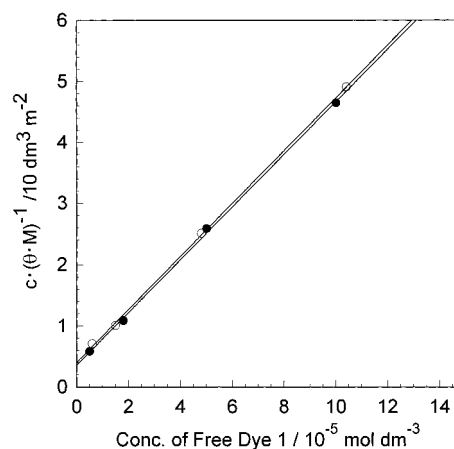
Figure 8. Langmuir plots on the basis of eq 3 for the adsorption of dye 1 to cubic AgBr emulsion grains system at 40 (○) and 60 °C (●).
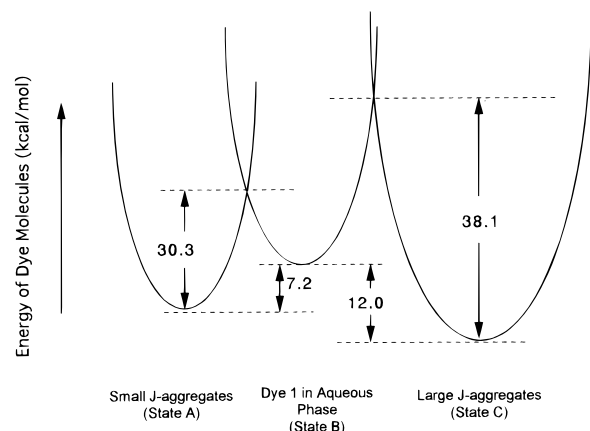
Figure 9. Potential energy diagram of dye 1 molecules in various states in octahedral AgBr grains. State A: Dye molecules in J-aggregates which were composed of 10 molecules on the average according to the estimation on the basis of eq 4. State B: Monomeric dye molecules in an aqueous gelatin solution. State C: Dye molecules in J-aggregates which were composed of 21 molecules on the average according to the above estimation.

Figure 9 shows the potential energy diagram of dye 1 in various states, which was derived from the activation energy of the desorption of dye 1 from AgBr grains and the heat of adsorption of dye 1 to the grains. This energy diagram supports the growth mechanism of J-aggregates of dyes on AgBr grains and the behavior of dyes in an emulsion as proposed in the previous paper.[5] Namely, the adsorption of dyes to silver halide grains is reversible, and dye molecules move on the grain surface through the repetition of their adsorption and desorption. The energy diagram also indicates that dye molecules in larger J-aggregates are more stable than those in smaller ones and that J-aggregates grow as a result of the movement of dye molecules from smaller aggregates to larger ones through the repetition of their desorption and adsorption. In the above-stated growth mechanism, the rate-determining step for the movement of dye molecules is their desorption from the grain surface. Since the activation energy for the desorption was rather high, stirring of a dyed emulsion at high temperature for long period promoted the movement of dye and resulted in the formation of large and stable J-aggregates on AgBr surface.

Table 2 indicates that the above-stated growth mechanism was consistent with the observed values of ΔG. Although the effect of ΔH promoted the movement of dye molecules from smaller aggregates to larger ones, the effect of ΔS promoted the movement in the opposite direction. It turned out from the value of ΔG that the effect of ΔH overcame that of ΔS.

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TABLE 2: Change of Thermodynamic Parameters for Adsorption of Dye 1 to AgBr Emulsion Grains

crystal face	ripening condition	K, 10^5 M^{-1}	ΔH, kcal/mol	ΔG, kcal/mol	ΔS, eu
(111)	40 °C, 20 min	7.63	−7.2	−9.0	5.8
(111)	60 °C, 20 min	16.5	−12.0	−10.1	−5.7
(100)	40 °C, 20 min	3.21	−9.6	−8.5	−3.5
(100)	60 °C, 20 min	3.33	−12.8	−9.0	−11.4

Namely, it is considered that the above-stated growth mechanism was relevant from a thermodynamic point of view.

3.5. Absorptivity of Dye to Silver Halide Grains with Crystal Habit. The heat of adsorption ($-\Delta H$) of dye 1 to octahedral AgBr grains was by about 1 kcal/mol smaller than that of the dye to the cubic grains. This result did not seem to coincide with the fact that the adsorptivity of dye 1 was larger to octahedral AgBr grains than to cubic ones.[12] By taking into account the facts that the average size of J-aggregates of dye 1 were larger on cubic grains than on octahedral ones under the same adsorption condition and that the effect of ΔS promoted the movement of dye 1 molecules from larger aggregates to smaller ones, it is considered that dye 1 molecules were inclined to be adsorbed rather to the octahedral grains than to the cubic ones, in spite of the fact that the heat of the adsorption of the dye to the octahedral grains was smaller than that to the cubic ones. The above-stated consideration was consistent with the observed values of ΔG.

4. Conclusions

1. A cross-linked macroporous polystyrene resin was found to be an appropriate adsorbent for sensitizing dyes in silver halide emulsions and provided a new method for the investigation of the desorption process of dyes from silver halide grains.

2. The desorption rate of a dye did not depend on its residual concentration on the grain surface.

3. The growth mechanism of J-aggregates of dyes through the repetition of their desorption and adsorption on silver halide grains was supported by the potential energy diagram of a dye in various states in an octahedral AgBr emulsion on the basis of the activation energy for the desorption and the heat of the adsorption of the dye to the grains.

4. The growth mechanism of J-aggregates and adsorptivity of dye 1 to AgBr grains with different crystal habits could be well explained by thermodynamic parameters.

References and Notes

(1) Jelley, E. E. *Nature* **1936**, *138*, 1009.
(2) Steiger, R.; Aebischer, J. N.; Haselbach, E. *J. Imaging Sci.* **1991**, *35*, 1.
(3) Tani, T.; Suzumoto, T. *J. Appl. Phys.* **1991**, *70*, 3626.
(4) Seki, K.; Araki, T.; Ito, E.; Ouchi, K.; Narioka, S.; Yokoyama, T.; Ohta, T.; Watanabe, S.; Matsunaga, A.; Tani, T. *J. Imaging Sci. Technol.* **1993**, *37*, 589.
(5) (a) Tani, T. *J. Imaging Sci.* **1985**, *29*, 165. (b) Tani, T. *J. Imaging Sci.* **1990**, *34*, 143.
(6) Berry, C. R.; Skillman, D. C. *Photogr. Sci. Eng.* **1962**, *6*, 159.
(7) Herz, A. H.; Danner, R. P.; Janusonis, G. A. *Adsorption from Aqueous Solution*; Advances in Chemistry Series 79; American Chemical Society: Washington, DC, 1968; p 173.
(8) Eucken, A.; Grundriss, D. *Phys. Chem.* **1948**, *6*, 355.
(9) Herz, A. H.; Helling, J. O. *J. Colloid Sci.* **1948**, *22*, 391.
(10) Tani, T.; Kikuchi, S. *J. Photogr. Sci.* **1969**, *17*, 33.
(11) Knapp, E. W. *Chem. Phys.* **1984**, *85*, 73.
(12) Mifune, H. Crystal-Face Selectivity of Adsorption of Cyanine Dyes to Silver Halide Grains. In the preprint book of The Annual Meeting of Society of Photographic Science and Technology, Japan, May 28, Tokyo, 1996.