The Mechanism of Cyanine Sensitizing Dye Adsorption on AgBr Crystals

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Introduction

Spectral sensitization is an important technology that renders silver halide crystals sensitive to the wavelengths of light longer than that of blue light. Spectral sensitization results from the adsorption of sensitizing dyes onto silver halide crystals. Sensitizing dyes are usually dissolved in solvent or dispersed in a dispersion medium, and are added to emulsions containing silver halide crystals. But, unlike the equilibrium state of adsorption, little data have been aquired about the process of sensitizing dyes' adsorption onto silver halides. We reported earlier that the adsorbing mechanism of some anion dye has a close relationship to the dye's conformation on the silver halide crystals[1]. In this study, we report the effects of N-substituents in the dye molecules on the adsorption mechanism of cyanine dyes onto silver halide crystals.

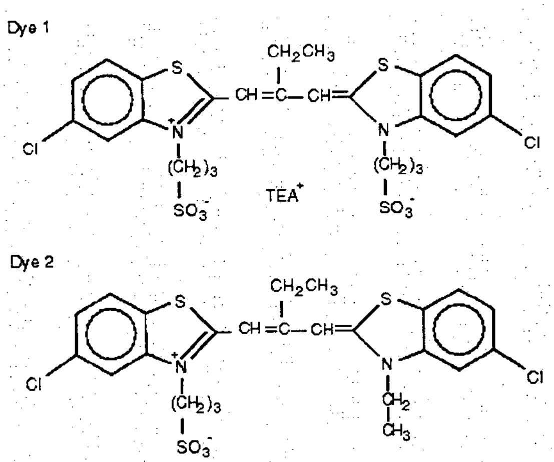

Fig. 1 Sensitizing Dyes 1 and 2

Measurement of dye adsorption rates

Sensitizing dyes dispersed in gelatin, shown in Fig. 1, were added to emulsions containing octahedral AgBr crystals 1.1 μm in size and grown in gelatin. Reflection spectra of the emulsions, which change as dye is adsorbed onto the AgBr crystals, were measured using a diode array detector spectrometer (Otsuka Electronics Co., Ltd. MCPD-1000), at durations less than one second. Changes in the amount of dye adsorbed (the adsorption rates) were determined from the spectra.

Mechanism of adsorption of Dye 1

The change of the spectrum when Dye 1 was added to the AgBr emulsion is shown in Fig. 2. The main peak, which was observed from just after the addition of the dye to the end of adsorption, is assigned to the J-aggregate of Dye1 on the AgBr crystals, showing that Dye1 adsorbs on the crystals and begins to form the J-aggregate quickly. Using the Kubelka-Munk equation, $[(1-R_{\infty})^2/2R_{\infty}]$ at the wavelength of maximum $-\log(R_{\infty})$ were plotted against time in Fig. 3. The

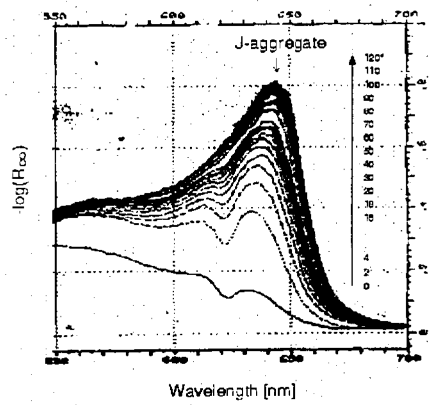

Fig. 2 Time-dependent adsorption spectra of Dye1/AgBr Oct.

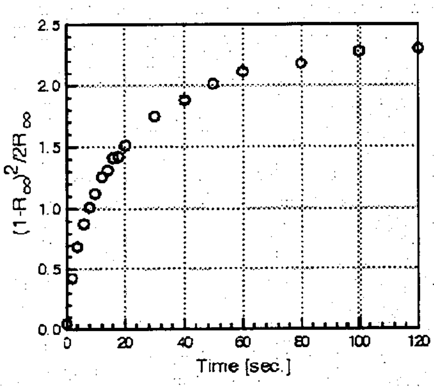

Fig. 3 Time-dependence of $(1-R_\infty)^2/2R_\infty$ at 41℃

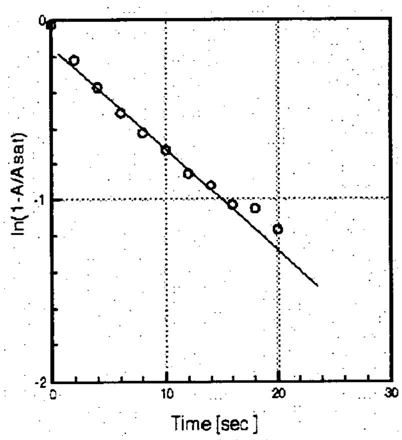

Fig. 4 Plots to calculate adsorption rate constant(k) at 41℃

expression $[(1-R_\infty)^2/2R_\infty]$ expresses a value which is in proportion to the amount of adsorbed dye. It increases quickly just after the addition of the dye, but the rate of increase then slows and stops 2.3, which is considered to be the equilibrium value. This rate does not depend on the amount of dye added.

From these observations, we suggest the following mechanism adsorption for Dye 1:

(1) Most of the molecules of the dye added to the emulsion immediately form particles, which cannot be adsorbed onto the AgBr crystals

(2) However, those few dye molecules which remain monomers go into solution in the emulsion, and are adsorbed, forming J-aggregates on vacant sites on the AgBr crystal surfaces.

(3) As these monomer dye molecules are adsorbed onto the AgBr crystals, their absence from the solution now allows monomers to break off from the dye particles, thus providing a constant supply of sensitizing dyes for adsorption.

We assume that the rate determining step is (2), with the rate of adsorption expressed as follows:

$A=Asat(1-e^{-kt})$

A: amount of adsorbed dye(substituted by $[(1-R_\infty)^2/2R_\infty]$)

Asat: satulated amount of adsorbed dye(substituted by 2.3)

k: rate constant

t: time

To establish the validity of the above equation, log(1-A/Asat) was plotted against time in Fig. 4. The plot gave a straight line, thus confirming the equation's validity. From the slope of the graph, the rate constant was calculated to be 4.3×10^{-2}[sec.$^{-1}$] at 41℃. In Fig. 5, log k was

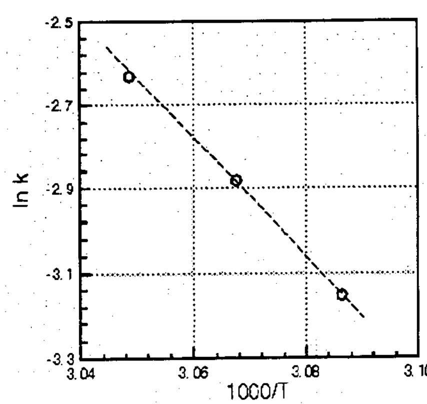

Fig. 5 Arrhenius plots to calculate activation energy

plotted against 1000/T (T: absolute temperature). The plot gave a straight line, from which activation energy (Ea) was calculated to be 28 kcal/mol.

Mechanism of adsorption of Dye 2

We measured the adsorption rate of Dye2, in the same manner as with Dye 1. Dye 2 adsorbs on the crystals and forms the J-aggregate quickly, like Dye1. But, unlike Dye 1, the adsorption rate does depend on the amount of dye added, as shown in Fig. 6. In Fig. 7, we plotted the initial adsorption rate, which is calculated from the tangent shown in Fig. 6, against the amount of dye added. The plot gave a straight line, indicates that Dye 2's adsorption rate is proportional to the amount of dye added. In addition, we determined that Dye 2's solubility in water is very low, indicates that Dye 2 exists in the form of small particles.

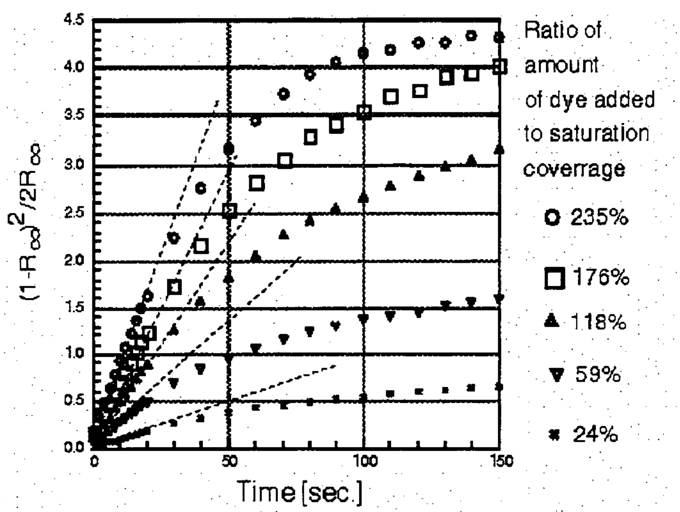

Fig. 6 Dependence of adsorption rate of Dye 2 on amount of dye added

From these observations, we considered two possible adsorption mechanisms for Dye 2:

A) Dye 2 adsorbes onto the AgBr crystals in particle form. As the amount of added dye increases, the frequency of dye crystal contact increases, thus increasing the adsorption rate.

B) Dye 2 does not adsorb onto the AgBr crystals in particle form, but in monomer form. Because of Dye 2's low monomer solubility, particle dissolution is the rate determining step, with the adsorption rate depends on the available total dye particle surface area. Thus, increasing the amount of dye added raises the rate of adsorption.

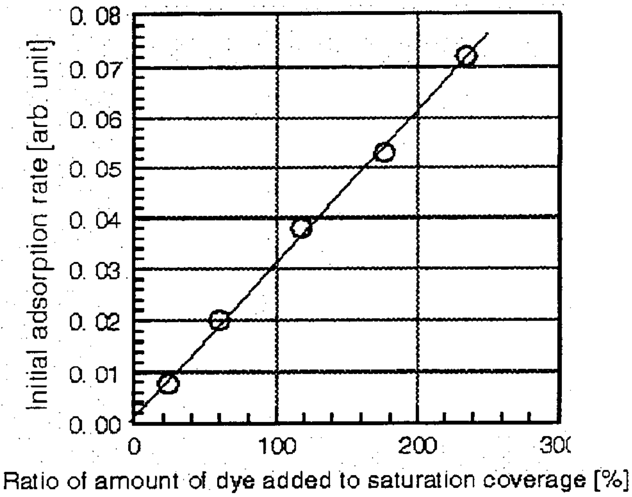

Fig. 7 Dependence of initial adsorption rate of Dye 2 on amount of dye added

To determine which mechanism was more likely, we studied the adsorption rates of Dye 2 in emulsions in which we varried AgBr crystal concentrations by increasing the emulsions' gelatin volume, but maintained the same ratio of

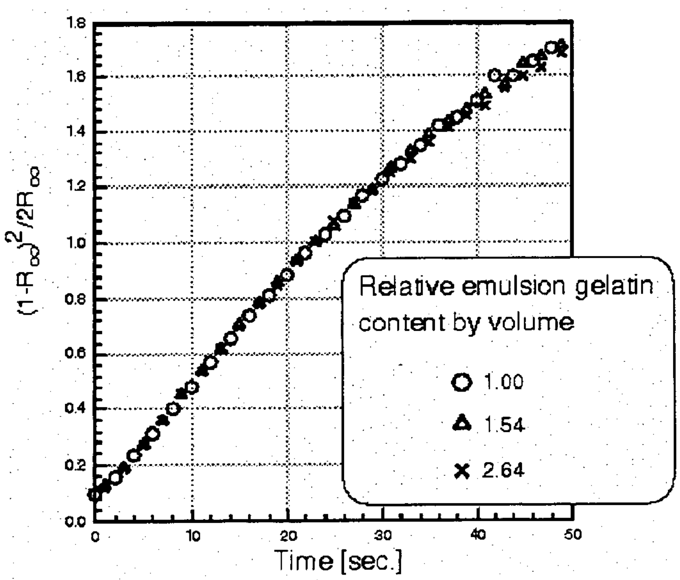

Fig. 8 Dependence of adsorption rate of Dye 2 on concentration of AgBr in emulsion

added dye to AgBr crystals. If mechanism (A) were operative, we would expect to see the adsorption rate rise or fall with the AgBr concentration. Fig. 8, however shows that no such changes resulted, so that mechanism (B) is more likely.

Conclusion

Measurement of the adsorption rate of sensitizing dyes has revealed that changing the N-substituents of sensitizing dyes molecule can change the adsorption rate of the dye onto silver halide crystals by changing the rate determining step.

1) H. Ando, N. Ohara, H. Masutomi; *IS&T's 49th Annual conference* (1996) pp. 233