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Examination of Relative Quantum Yield of Spectral Sensitization as Efficiency of Electron Transfer from Excited Dyes to Silver Halides[‡]

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The relative quantum yield of spectral sensitization (ϕ_r) is given by the ratio of the quantum yield of latent-image formation upon excitation of sensitizing dyes to that upon excitation of silver halide grains, being regarded as the quantum yield of the light-induced electron transfer from sensitizing dyes to silver halide grains (ϕ_s) under the assumption that the behavior of positive holes is independent of whether they are created by the excitation of sensitizing dyes or by the excitation of silver halide grains. We point out, however, that in some special cases ϕ_r is not equal to ϕ_s, since the behavior of positive holes created in sensitizing dyes is different from that of positive holes created in silver halides. The condition is described for the measurement of ϕ_r that is equal to ϕ_s.

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Introduction

The quantum yield of spectral sensitization is an important quantity for examining the condition and mechanism of spectral sensitization in photography.[1,2] Since it is now accepted that spectral sensitization takes place as a result of electron transfer from sensitizing dyes in the lowest excited singlet state to silver halide grains,[1,3a,b] the quantum yield of spectral sensitization is the quantum yield of the light-induced electron transfer (ϕ_s). The relative quantum yield of spectral sensitization (ϕ_r)[4] is usually given by the ratio of the quantum yield of the latent-image formation on the excitation of sensitizing dyes to that on the excitation of silver halide grains, and is successfully used for the study of spectral sensitization.[1–3a,b] However, it is clear from the above definition that ϕ_r is equal to ϕ_s only when the behavior of positive holes created by the excitation of sensitizing dyes is the same as that of positive holes created by the excitation of the silver halide.

The realization of the condition where $\phi_r = \phi_s$ has been proved for many cases by several observations. It is known that ϕ_r is independent of the presence of chemical sensitization centers,[5,6a–g] in spite of the fact that chemical sensitization centers can interact with positive holes. It is known that sensitizing dyes in the excited state can inject both electrons and positive holes into silver halides,[7a-d] bringing about spectral sensitizations of latent-image formation by injected electrons and destruction of fog centers by injected positive holes.[8a,b] The observation that ϕ_r for the spectral sensitization of latent-image formation was nearly the same as ϕ_r for the spectral sensitization of destruction of fog centers for most sensitizing dyes indicated that $\phi_r = \phi_s$ for the latent-image formation and the destruction of fog centers.[9] The blue sensitivity of spectrally sensitized fine AgBr emulsion grains was independent of the presence of reduction sensitization centers when the exposed film samples were immersed in water to deactivate dye positive holes just after the exposure to blue light,[10] indicating that almost all the positive holes created by the light absorption of the grains were captured by the dye before they were captured by reduction sensitization centers.

Recently, Spitler[11] raised the question of $\phi_r = \phi_s$. In this article, systematic considerations are made and experiments are conducted to examine if there is any condition under which ϕ_r is not equal to ϕ_s.

Relative Quantum Yield of Spectral Sensitization

The relative quantum yield of spectral sensitization (ϕ_r) is given by the ratio of the number of quanta absorbed only by the silver halide necessary to produce a specified developed density to the number of quanta absorbed only by the dye at a wavelength λ within its absorption band required to produce the same density, as described by the following equation:[4]

$$\phi_r = (400E_{400}A_{400})/\,(\lambda E_\lambda A_\lambda), \tag{1}$$

where E_{400} is the incident radiation energy at 400 nm required to produce the specific density, A_{400} is the fraction of this radiation absorbed by the emulsion coating, and E_λ and A_λ are the corresponding quantities for wavelength λ nm. Thus, $400E_{400}/\lambda E$ gives the ratio of the number of the incident photons at 400 nm required to produce the specific density to the number of incident photons at λ nm to produce the same specific density. For the measurement of ϕ_r,[1,2,4] the number of quanta absorbed by the AgBr and AgBrI is measured at 400 nm, a wavelength not absorbed by most sensitizing dyes. The value of ϕ_r is related to the quantum yield of the light-induced electron transfer (ϕ_s), the quantum yields of the latent-image formation by free electrons produced by the incident radiation of 400 and λ nm ($\phi_{LI,400}$ and $\phi_{LI,\lambda}$, respectively), the rate constants of the electron transfer and competing deactivation channels (k_s and k_L, respectively), and the rate constants of radiative and nonradiative recombination processes (k_r and k_{nr}, respectively), as follows:[1,2]

$$\phi_r = \phi_s(\phi_{LI,\lambda}/\phi_{LI,400}), \tag{2}$$

$$\phi_s = k_s/(k_s + k_L) = k_s/(k_s + k_r + k_{nr}). \tag{3}$$

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Although the right side of Eq. 3 is originally defined for the efficiency of the electron transfer, it should be valid because the light-induced electron transfer for spectral sensitization took place from dye molecules in the excited singlet state, which were produced with the probability of unity by light absorption by the dye molecules.[12] Thus, $\phi_r = \phi_s$ only when $\phi_{LI,\lambda} = \phi_{LI,400}$. Note that all of the positive holes are at first trapped by sensitizing dyes upon the excitation of the dyes, whereas all of the positive holes are at first in the valence band of silver halide upon the excitation of the silver halide. Therefore $\phi_r = \phi_s$ under the condition where all the positive holes that appeared in the valence band of the silver halide are then trapped by the dyes or under the condition where positive holes can be rapidly released from dyes, going everywhere in a dyed grain even in the presence of positive hole traps such as reduction sensitization centers (Ag_2),[13,14] and the behavior of positive holes is thus independent of whether they are created by the excitation of dyes or by the excitation of silver halides. This situation is illustrated in Fig. 1.

On the basis of the above consideration, it is predicted that there could be two special conditions under which ϕ_r would deviate from ϕ_s, as described below[1,15]:

1. Deviation I: In emulsion grains with hole-trapping silver centers (Ag_2), it is considered that $\phi_{LI,\lambda}$ is smaller than $\phi_{LI,400}$ in the presence of those dyes whose HOMO levels are too high for positive holes to be rapidly released. Thus, some positive holes produced in the valence band of the grains by the excitation at 400 nm could react with Ag_2 before they were captured by the dye molecules, whereas positive holes produced on the dyes by the excitation at λ nm could hardly be released to react with Ag_2. This situation is illustrated in Fig. 2.

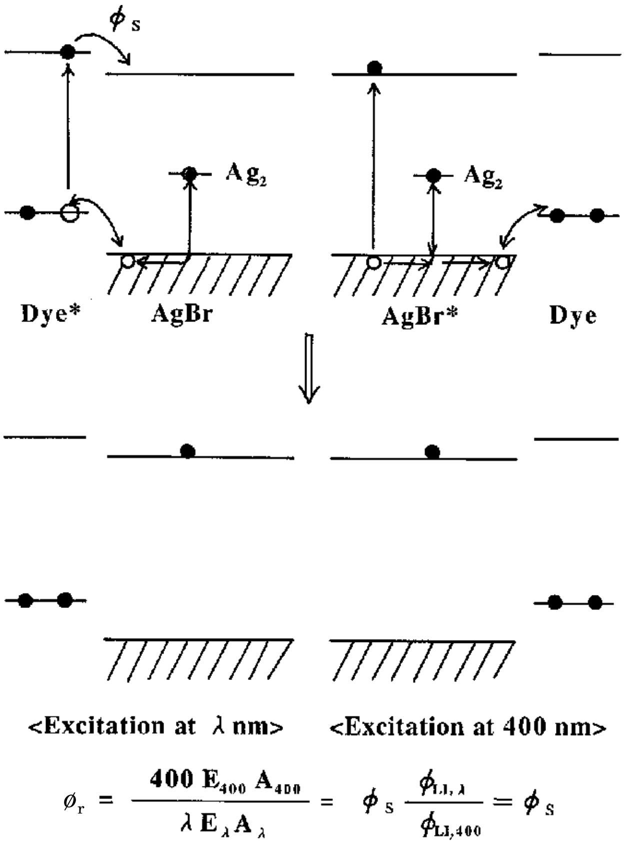


Figure 1. Behavior of electrons and positive holes of dyed emulsion grains in the presence of hole-trapping silver clusters (Ag_2) on the excitations at λ and 400 nm. The HOMO of a dye is not so high as to restrict the behavior of positive holes, and the grain size is smaller than the diffusion length of positive holes. Positive holes can therefore go everywhere in a grain, and their behavior is independent of whether they are created in dye molecules on excitation at λ nm or in silver halide emulsion grains on excitation at 400 nm.

2. Deviation II: In emulsion grains that are free from hole-trapping silver centers and too large for all the positive holes in the interior to reach the grain surface, $\phi_{LI,400}$ was smaller than $\phi_{LI,\lambda}$ for those dyes whose HOMO levels are too high for positive holes to be rapidly released. It is known that positive holes can be deactivated at the surface of silver halides.[16a,b] However, in large grains, some positive holes produced in the interior cannot reach the grain surface and are thus subjected to recombination with photoelectrons in the interior of the grains. This situation is illustrated in Fig. 3.

The above deviations result from the difference between behavior of positive holes in spectrally sensitized emulsions on excitation of silver halide grains and on excitation of sensitizing dyes. It is known that the microwave photoconductivity of spectrally sensitized silver halide grains is proportional to the concentration of photoelectrons, which are free from the behavior of positive holes.[1,17] Therefore we consider ϕ_r to be always equal to ϕ_s when ϕ_r can be determined by the microwave photoconductivity instead of by photographic sensitivity.

Experiments

The molecular structures of the dyes used in this study are shown in Fig. 4. The electronic energy levels of the

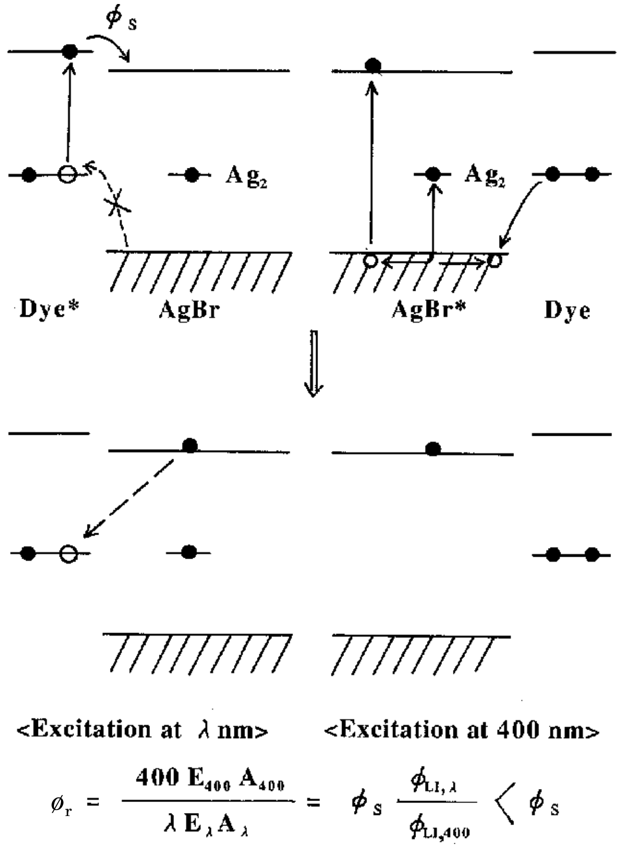
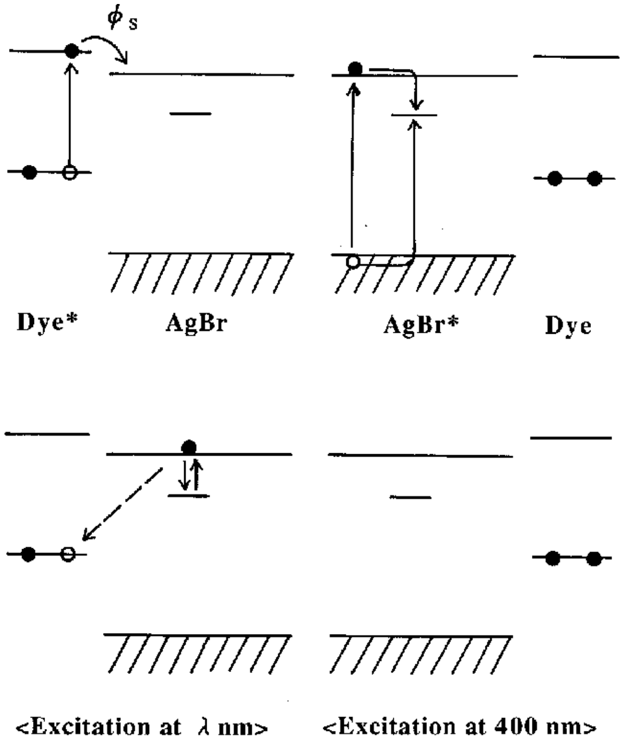


Figure 2. Behavior of electrons and positive holes of dyed emulsion grains in the presence of hole-trapping silver clusters (Ag_2) on the excitations at λ and 400 nm. The HOMO of the dye is very high, and positive holes trapped by dye molecules are hardly released.



$$\phi_r = \frac{400\, E_{400}\, A_{400}}{\lambda\, E_\lambda\, A_\lambda} = \phi_S \frac{\phi_{LI,\lambda}}{\phi_{LI,400}} > \phi_S$$

Figure 3. Behavior of electrons and positive holes of dyed emulsion grains in the absence of hole-trapping silver clusters (Ag_2) on the excitations at λ and 400 nm. The HOMO of the dye is high, and positive holes are trapped primarily by dye molecules. The grain size is much larger than the diffusion length of positive holes.

highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated and shown in Fig. 5 on the basis of Eqs. 4 and 5,[1,2] which have been widely and successfully used for studies on the relation between the spectrally sensitizing ability and electronic energy levels of sensitizing dyes,[1,2] as shown below:

$$\varepsilon_{HO} = -E_{OX} + C, \tag{4}$$

$$\varepsilon_{LU} = -E_R + C, \tag{5}$$

where ε_{HO} and ε_{LU} are the electronic energy levels of HOMO and LUMO of a dye, respectively; E_{OX} and E_R are oxidation and reduction potentials of the dye, respectively; and C is an electrochemical constant. Equations 4 and 5 can be theoretically and experimentally verified by use of a molecular orbital method,[1,2] and experimentally confirmed by means of ultraviolet spectroscopy, which determines directly the electronic energy levels of dyes.[1,2,18a–e]

There are some problems to be considered regarding the validity of Eqs. 4 and 5. One problem is that dyes are in contact with silver halides in emulsions, whereas silver halide is absent in solutions for the measurement of E_R and E_{OX}. Another problem is that dyes in solutions for the measurement of E_R and E_{OX} are monomeric, whereas dyes in emulsions are more or less aggregated. There was some difference in the form of aggregates among the dyes studied. Dyes 1–3 formed J-aggregates on the cubic AgBr emulsion grains used in this study, whereas Dye 4 did not.

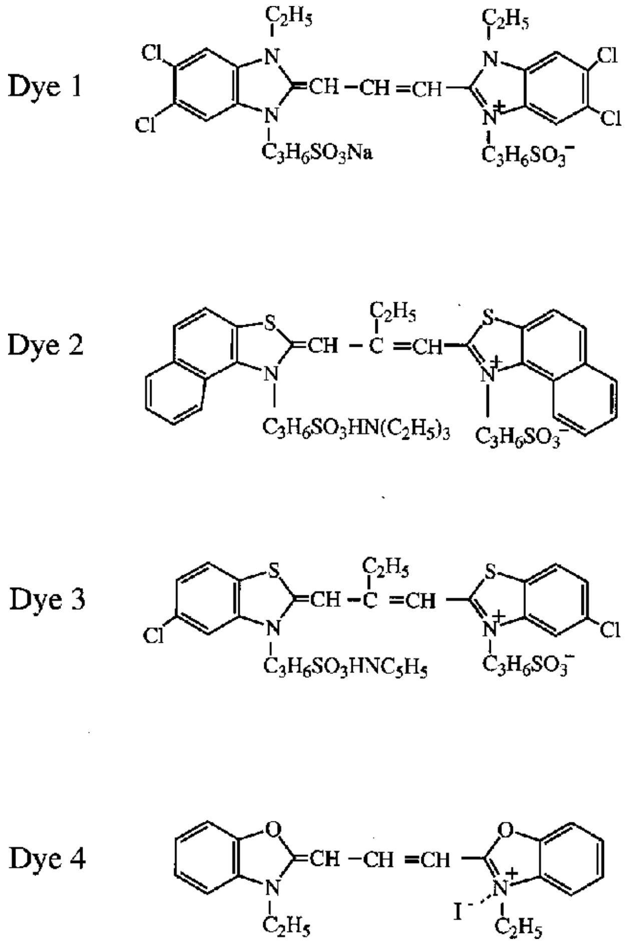


Figure 4. The molecular structures of the dyes studied in this article.

In spite of these problems, it turned out through studies by many groups of investigators that the correlation between photographic phenomena and electronic energy levels as estimated by Eqs. 4 and 5 was fairly good among various dyes with differences in the form of aggregates.[1,19a-c] The reasons for the realization of the correlation are as follows.

The measurements of E_R and E_{OX} for dye molecules that were not in contact with silver halides were not a big problem in terms of the validity of Eqs. 4 and 5, owing to the fact that the nature of the interaction of dye molecules with silver halides, as well as the nature of their interaction with solvents, was physical.[1]

In many cases, dye molecules on the surface of silver halides in emulsions can be regarded as condensed systems, which more or less contain aggregated dye molecules with split transition states, and the transition state with the smallest energy is allowed in J-aggregates and forbidden in H-aggregates, whereas the transition with the largest energy is forbidden in J-aggregates and allowed in H-aggregates.[1] According to Kasha's law,[12] the transition states with the smallest energy are considered to play a predominant role in spectral sensitization regardless of the form of their aggregates. The above consideration would provide the reason why the good correlation between photographic phenomena and the electronic energy levels of dyes could be realized on the basis of Eqs. 4 and 5, since the degree of the splitting in the transition energy did not differ too much among dyes with similar molecular structure, regardless of the form of their aggregates.

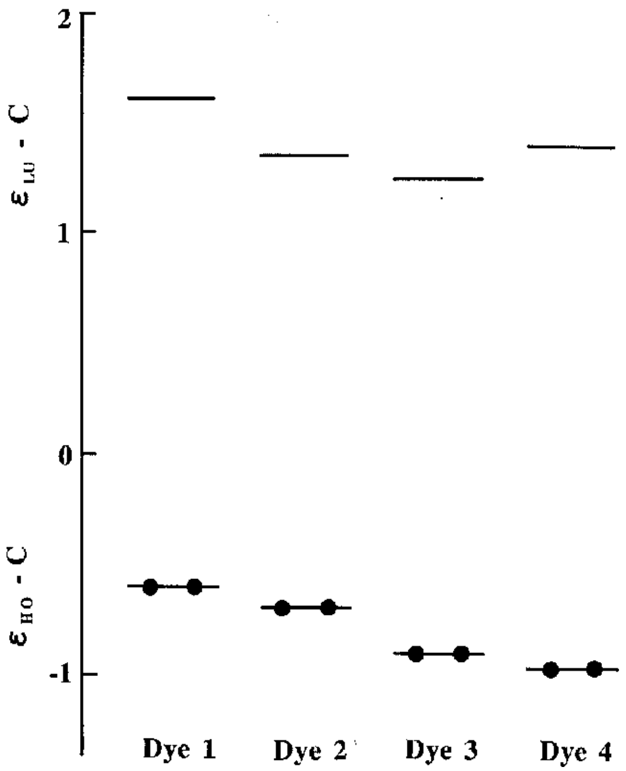


Figure 5. The electronic energy levels of HOMO and LUMO (ε_{HO} and ε_{LU}) of Dyes 1–4, which were estimated according to Eqs. 4 and 5.

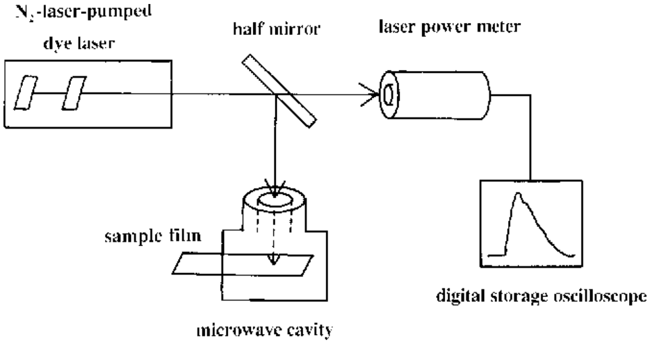


Figure 6. The outline of the apparatus for the measurement of microwave photoconductivity in this study.

Two series of cubic AgBr emulsion grains were prepared by means of the controlled double-jet (CDJ) method.[20–22] In Series A, cubic AgBr grains with an equivalent circular diameter of 0.6 µm were prepared in solutions with a temperature of 70°C, silver potential of 150 mV versus SCE, and pH of varied values. The finished emulsions contained 88.5 mmol of AgBr and 10.2 g of gelatin/100 g and had a pH value of 6.6, pAg value of 8.5 at 40°C, and specific gravity of 1.19. Reduction sensitization was performed by adding thiourea dioxide to the emulsions, which were then digested at 60°C for 60 min.

The cubic AgBr emulsions of Series B were prepared by the CDJ method in solutions with a temperature of 70°C, silver potential of 150 mV versus SCE, and pH of 2.5. The grain size was varied. The values of the pH, pAg, and specific gravity of the finished emulsions were the same as those of the first series of emulsions.

Methanolic solutions of dyes were added to the emulsions, which were coated on TAC film bases at 43 mg AgBr/dm^2 and 52 mg gelatin/dm^2. For the measurement of $ø_r$, a film sample was exposed for 10 or 100 s to a tungsten lamp (color temperature: 2854 K) through a Schott bandpass filter and a wedge. The wavelengths of the lights to excite AgBr and a dye were 400 and λ nm (i.e., the wavelength at the maximum of the absorption band of the dye), respectively. The light intensity was measured by an EG&G Model 550 radiophotometer. The exposed film sample was developed for 10 min at 20°C by the surface developer MAA-1.[23] The optical density of a processed film sample was measured by a Fuji densitometer to give E_{400} and E_λ, which were required to give the optical density of 0.1 above fog with exposures to 400 and λ nm, respectively. The difference in covering power among different-sized emulsion grains did not have any significant influence on the comparison of $ø_r$ for a dye among those grains, because the gamma of the characteristic curve of each emulsion on its exposure to 400 nm was nearly the same as that on its exposure to λ nm.

The absorbances of a film sample at 400 and λ nm (i.e., A_{400} and A_λ, respectively) were obtained according to the following equation:

$$A = 1 - T - R, \qquad (6)$$

where T and R are the diffuse transmittance and reflectance of a film sample, respectively. The measured values of E_{400}, E_λ, A_{400}, and A_λ were put into Eq. 1 to give $ø_r$.

The apparatus for the measurement of microwave photoconductivity, which was developed by Kaneda,[24] is outlined in Fig. 6. The light source used was an N_2-laser-pumped dye laser. The N_2 laser and dye laser used were Molectron Corporation Models UV24 and DL14, respectively. The microwave cavity and its accessories were transferred from a JEL Model ME electron spin resonance spectrometer. A film sample was subjected to measurements of the microwave photoconductivity by use of the above apparatus at room temperature. The signal was detected and stored by an Iwatsu Electric Model DS-6612C digital storage oscilloscope. A light pulse was divided in two by a half mirror. One half was guided to a Molectron Corporation Model J3-09 laser power meter for the measurement of its intensity by a digital storage oscilloscope. The other was guided to a film sample in a microwave cavity for the measurement of its microwave photoconductivity. Figure 7 shows an example of a signal measured by the above apparatus.

Results

Figure 8 shows the relative sensitivities of reduction-sensitized and dyed emulsions (Series A) that were prepared at a pH of 2. The abscissa indicates the amount of thiourea dioxide used for reduction sensitization. Each emulsion contained Dye 1 in an amount that could cover 30% of the surface of the emulsion grains when a dye molecule occupied 70 A^2 on the grain surface.[25] As seen in Fig. 8, the increase in the sensitivity by reduction sensitization was more pronounced for the exposure to 400-nm light to excite AgBr grains than for the exposure to 571-nm light to excite Dye 1. Accordingly, $ø_r$ of Dye 1 decreased with an increasing degree of reduction sensitization, as seen in Fig. 9.

Figure 10 shows the relative sensitivities of undyed and dyed emulsion grains (Series A) as functions of pH values of the reaction solution during their precipitations. The value of S_{400} of undyed emulsions increased with increasing pH values. Dyed emulsions contained Dye 1 in amounts that could cover 10 and 30% of the surface of the emulsion grains. Figure 11 shows the $ø_r$ of Dye 1 as a function of the

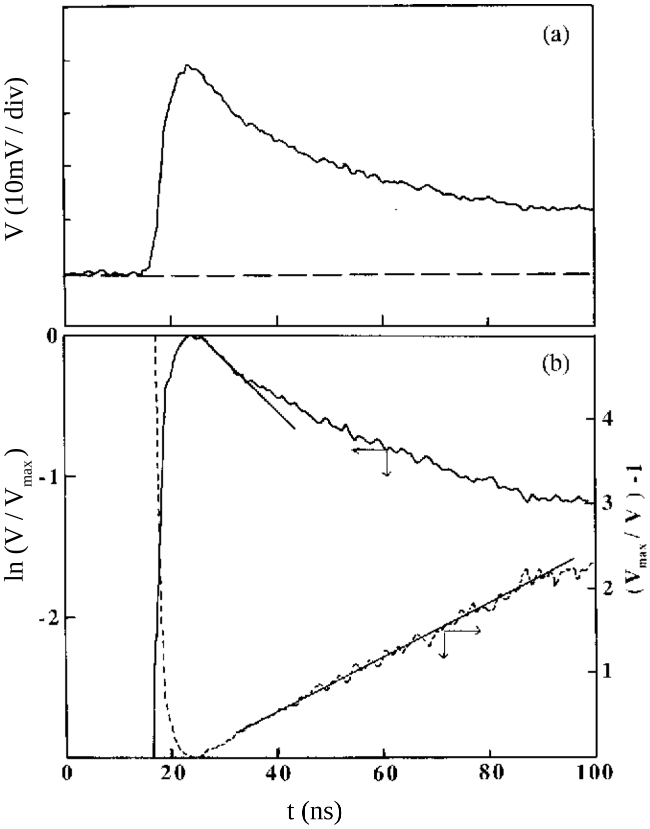


Figure 7. (a) A microwave photoconductivity signal and (b) its processing.

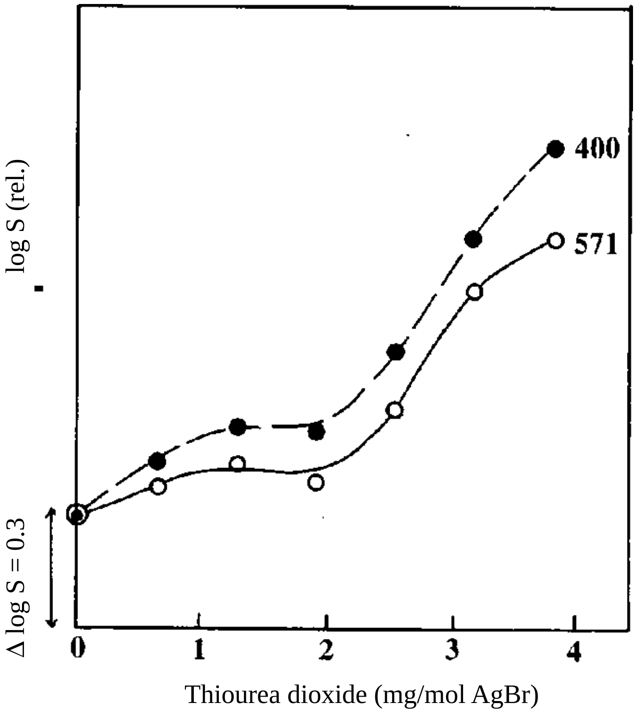


Figure 8. Sensitivities (S) of reduction-sensitized and dyed AgBr emulsions (Series A: prepared at pH 2) to 400- and 571-nm light as functions of the amount of thiourea dioxide used for the reduction sensitization.

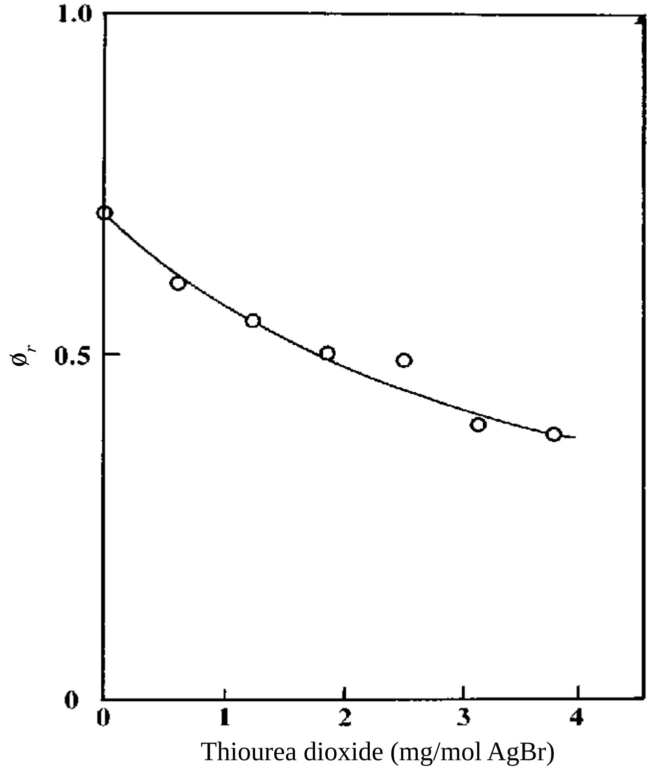


Figure 9. The values of ϕ_r of the dyed emulsions described in Fig. 8 as a function of the amount of thiourea dioxide used for the reduction sensitization.

pH values. As seen in this figure, ϕ_r decreased with increasing pH values.

Figure 12 shows the measured values of the signal peak height of the microwave photoconductivity of dyed emulsions (Series A) with reference to the intensity of the 575-nm laser pulse for its measurement as a function of pH values for the reaction solutions for the precipitation of the emulsion grains. Each emulsion contained Dye 1 in an amount that could cover 30% of the surface of the emulsion grains. As seen in this figure, the photoconductivity of the emulsions on the excitation of Dye 1 by a 575-nm laser pulse was nearly independent of the pH values. As indicated in the Relative Quantum Yield section, this result supports the idea that the deviation of ϕ_r from ϕ_s results from the difference of the behavior of positive holes in a spectrally sensitized emulsion on the excitation of silver halide grains from that of positive holes in the same emulsion on the excitation of sensitizing dyes, since the photoconductivity is proportional to the concentration of photoelectrons, being free from the behavior of positive holes.[1,17]

Figure 13 compares between values for ϕ_r of Dyes 1–4 in emulsions (Series A) prepared at pH 2 and pH 9. As seen here, the values of ϕ_r of Dyes 1 and 2 in the emulsions prepared at pH 9 were much smaller than those in the emulsions prepared at pH 2, whereas the values of ϕ_r of Dyes 3 and 4 in the emulsions prepared at pH 9 were nearly equal to those in the emulsions prepared at pH 2.

Figure 14 shows the relative sensitivities of dyed emulsions (Series B) as a function of the edge length of the emulsion grains. Each emulsion contained Dye 1 in an amount that could cover 10% of the surface of the emulsion grains. The sensitivity was expressed by the reciprocal of the product between exposure required to give an optical density of 0.1 above fog density and light absorbance for each

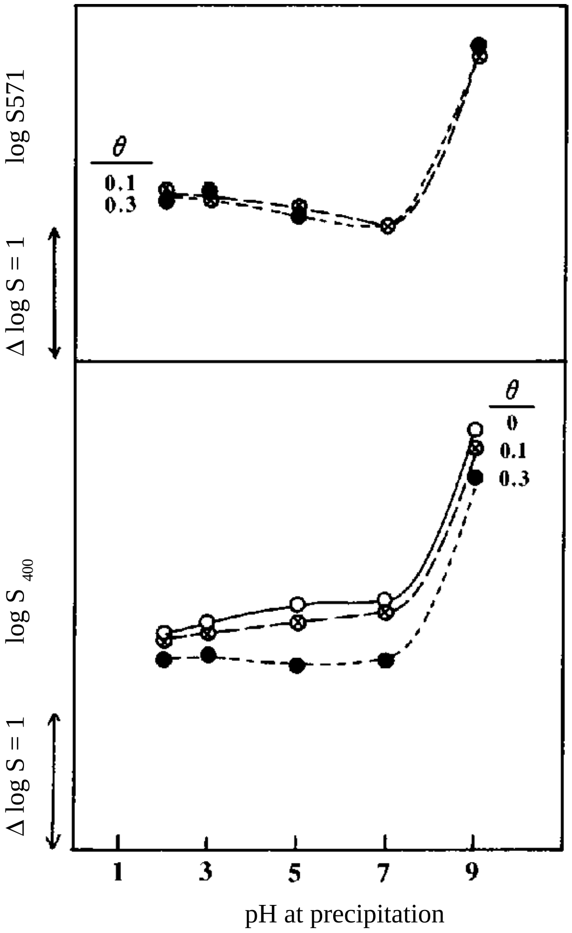


Figure 10. Sensitivities of AgBr emulsions (Series A) covered by Dye 1 to 400- and 571-nm light (S_{400} and S_{571}, respectively) as a function of pH of the reaction solution during the precipitation of the emulsion grains. The surface coverage of the grains by the dye (θ) was 0.1 and 0.3.

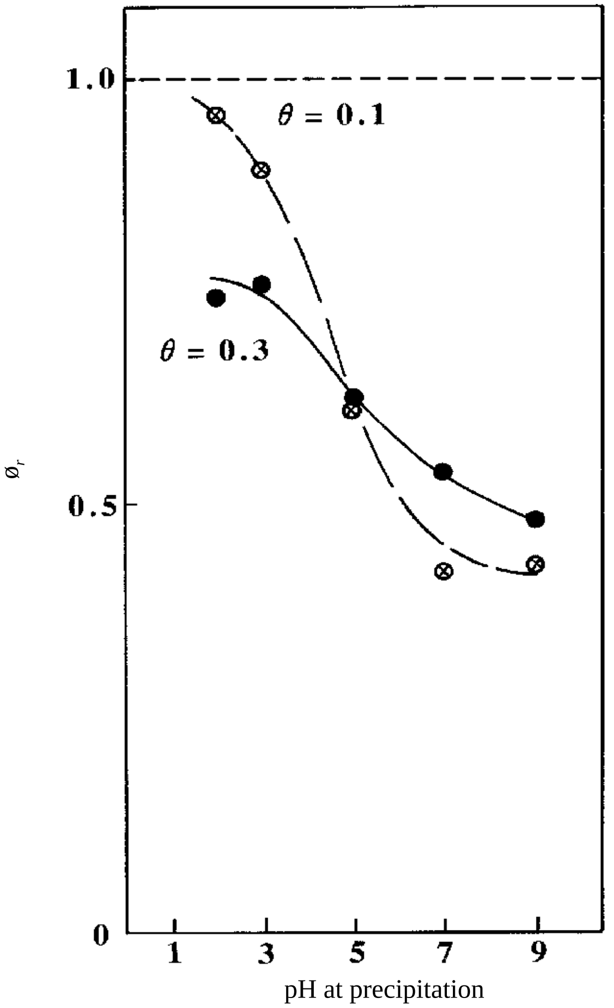


Figure 11. The values of ϕ_r for the dyed emulsions described in Fig. 10 as a function of pH of the reaction solutions during the precipitation of the emulsion grains.

film sample. The degree of increase in sensitivity due to the increase in the size of emulsion grains was more pronounced for the exposure to 571-nm light to excite Dye 1 than for the exposure to 400-nm light to excite AgBr grains. As seen in Fig. 15, the ϕ_r of Dye 1 increased with increasing grain size and became more than unity.

Discussion

To examine the predictions described in the Relative Quantum Yield section, two kinds of experiments were performed in this study. One set examined the effect of hole-trapping silver clusters on ϕ_r for dyes with variations in ε_{HO}, by use of emulsions of Series A. The other experiment examined the effect of grain size on ϕ_r for Dye 1 on emulsion grains of Series B, in which the concentration of hole-trapping silver clusters was assumed to be very low.

Hole-trapping silver clusters were formed on emulsion grains during the digestion of the emulsions in the presence of thiourea dioxide for their reduction sensitization and during their precipitation in reaction solutions with elevated pH. Pouradier pointed out that silver clusters could be formed on silver halide grains in emulsions and stabilized by gelatin when an aqueous solution of silver nitrate was added to a reaction solution with elevated pH during the precipitation of the grains.[26] Illingsworth precipitated emulsion grains in a reaction solution with low pH to avoid the formation of such silver clusters.[27] This consideration could be supported by the similarity of the observed phenomena shown in Figs. 10 and 11 to those shown in Figs. 8 and 9.

It is known that ε_{HO} of Dye 1 is extraordinarily high among many sensitizing dyes.[8b,28] Dye 1 is therefore considered most suitable for the examination of the two types of deviations of ϕ_r from ϕ_s (i.e., Deviations I and II), as illustrated in Figs. 2 and 3.

The decrease in ϕ_r of Dye 1 with an increasing concentration of silver clusters on emulsion grains, as seen in Figs. 9 and 11, gave evidence of Deviation I, as illustrated in Fig. 2. Specifically, ϕ_r decreased with an increasing concentration of hole-trapping silver clusters, although ϕ_s and therefore the number of electrons transferred to the conduction band of AgBr grains from Dye 1 in the excited state should be independent of the concentration of hole-trapping silver clusters. This idea was evidenced by the microwave photoconductivity of those emulsion grains, as shown in Fig. 12. In emulsions with fine AgBr grains prepared at low pH, the concentration of silver clusters is considered to be very low, and ϕ_r was close to ϕ_s even for Dye 1.

As seen in Fig. 13, Deviation I was observed for Dyes 1 and 2, whose HOMOs are very high among sensitizing dyes,[8b,27] whereas Deviation I was hardly observed for Dyes 3 and 4. Although the ε_{HO} of Dye 4 is low, that of Dye 3 is fairly high among sensitizing dyes.[8b,28] Therefore ϕ_r is considered to be nearly equal to ϕ_s for many sensitizing dyes.

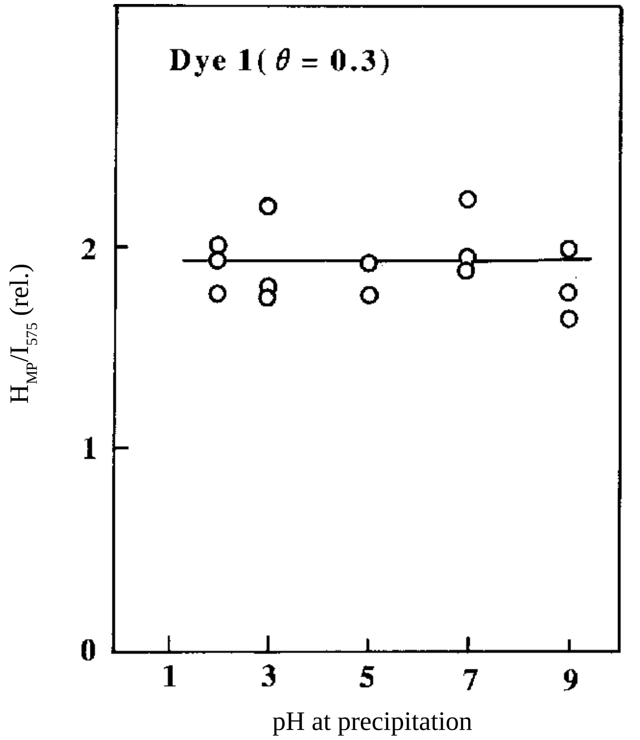


Figure 12. The signal peak heights of the microwave photoconductivity of emulsion grains of Series A covered by Dye 1 (H_{MP}) with reference to the intensity of 575-nm laser pulses for its measurement (I_{575}) as a function of the pH values of the reaction solutions during the preparation of the emulsions. The surface coverage of the grains by the dye was 0.3.

Attention should be paid to the measurement of ϕ_r of the dyes whose ε_{HO} values are very high.

According to the analysis of the dependence of photographic phenomena on the pH values of the reaction solutions for the preparation of the emulsions (Series A), the concentration of silver clusters in AgBr grains in emulsions (Series B) was considered to be very low, since they were prepared at low pH. Thus, Deviation II as illustrated in Fig. 3 was evidenced by the observation shown in Fig. 15. Namely, some positive holes created in the interior of the grains on excitation at 400 nm could neither reach the grain surface nor react with hole-trapping silver clusters; thus they were forced to recombine with photoelectrons before they were trapped by Dye 1 on the grain surface. Such an efficient recombination between photoelectrons and positive holes could be recognized as the cause for the inefficient formation of printout silver in large crystals of silver halides, in which positive holes as well as photoelectrons were created too deep in the interior to reach the surface of the crystal.[29a,b]

Conclusions

Deviations I and II were confirmed in this paper, although ϕ_r could be nearly equal to ϕ_s for many cases, as discussed in the analysis of the observation shown in Fig. 13.

To obtain ϕ_s from the measurement of ϕ_r, a recommendation should be made to use emulsion grains that are small and free from hole-trapping silver clusters. To obtain information about ϕ_s in a given emulsion, attention should be paid to the measurement of ϕ_r for dyes whose ε_{HO} values are very high. The measurement of the microwave photoconductivity[1,30a,b] and Dember effect[1,31a,b] of emulsion grains on the excitation of sensitizing dyes may be useful for the analysis of the above situation. ▲

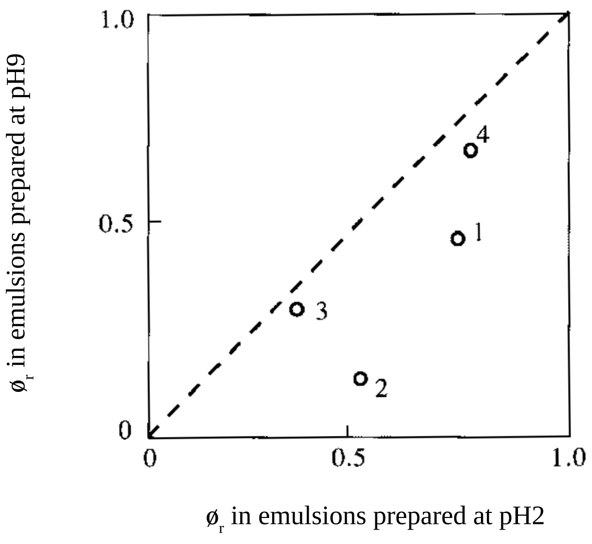


Figure 13. The comparison between ϕ_r for spectral sensitization of emulsion grains of Series A prepared at pH 2 and 9. The numbers in this figure refer to dyes in Fig. 4.

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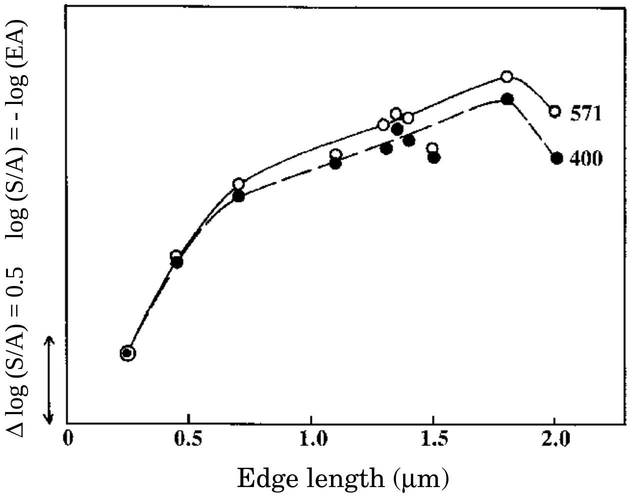

Figure 14. Sensitivity of emulsion grains of Series B covered by Dye 1 (S) with reference to light absorbance of each film sample (A) as a function of their average edge lengths.

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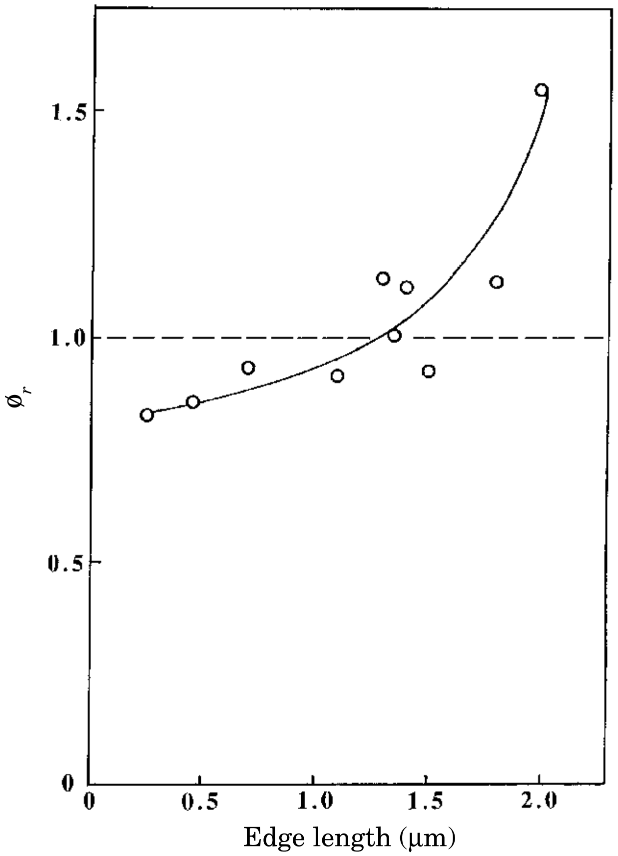

Figure 15. The value of ϕ_r for spectral sensitization of emulsion grains of Series B by Dye 1 as a function of their average edge length. The surface coverage of those grains by Dye l was 0.1.