JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 47, Number 1, January/February 2003

Silver Clusters of Photographic Interest: Formation of Silver Clusters During Precipitation of Silver Bromide Emulsion Grains

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The formation of silver clusters due to reduction of silver ions by gelatin during precipitation process of AgBr grains in emulsions was studied from the point of view that it should take place when the potential of the silver half-cell (E_{Ag}) was more positive than the potential of the gelatin half-cell (E_{Gel}) in a reaction solution. Although the sensitivities of the prepared emulsions were independent of E_{Ag} of the bulk reaction solutions, they increased with increasing pH values, and reached the sensitivities of the corresponding reduction sensitized emulsions and hydrogen hypersensitized ones. These results indicate that the formed clusters were reduction sensitization centers. It is proposed that silver cluster formation takes place, not in the bulk reaction medium, but in the region into which an aqueous solution of silver nitrate has been introduced for precipitation, since this is the only region where E_{Ag} is more positive than E_{Gel} in a reaction vessel.

Journal of Imaging Science and Technology 47: 78–83 (2003)

Introduction

Silver clusters play crucial roles in photographic processes.[1] In this series of papers,[2-7] studies have been made on the formation mechanism and properties of silver clusters on silver halide grains in photographic emulsions from various aspects. Silver clusters are formed on silver halide grains as the result of, not only the photolysis of the grains, but also the reduction of the grains by reducing agents.

It has also been described that silver clusters are formed as the result of the reduction of AgBr grains by gelatin in liquid emulsions,[3] i.e., silver digestion,[8] as represented by the following general reversible reaction.

$$\mathrm{Red} + n\mathrm{Ag}^+ \rightleftarrows nAg + \mathrm{Ox} + m\mathrm{H}^+ \tag{1}$$

where Red is reduced gelatin, *Ox* is oxidized gelatin, n is the number of electrons given up by the reduced gelatin, and m is the number of protons produced. Equation (1) can be separated into two half-cells, each of which has a characteristic potential associated with it. For the silver half-cell, E_{Ag}

$$\mathrm{Ag}^+ + \mathrm{e}^- \rightleftarrows \mathrm{Ag}, \tag{2}$$

and for the gelatin half-cell, E_{Gel}

$$\mathrm{Ox} + m\mathrm{H}^+ + \mathrm{ne}^- \rightleftarrows \mathrm{Red} \tag{3}$$

The cell potential for Eq. (1) is accordingly the difference between the potentials for the two half-cell reactions,

$$\Delta E = E_{Ag} - E_{Gel} \tag{4}$$

and the rate of silver cluster formation, d[Ag]/dt, should be given approximately by the electron flow from the gelatin half-cell to the silver half-cell, and expressed as follows,[9]

$$\mathrm{d[Ag]/d}t = [\mathrm{Red}]k^0_{Ox}\exp[(1-\alpha)nF\Delta E/RT] \tag{5}$$

where [Red] is the concentration of the reduced gelatin, k^0_{Ox} is the specific rate of the forward reaction in Eq. (1), α is the charge transport coefficient, and F is the Faraday constant. It was predicted from Eqs. (4) and (5) that Eq. (1) should proceed to the right when ΔE is positive, and this prediction was confirmed experimentally in a former study.[3]

We also reported that silver clusters were formed as the result of the reduction of AgBr grains by gelatin in dried emulsion layers.[4] In this case, it was demonstrated that the Fermi level of a dried gelatin layer was higher than that of AgBr. The above results were in concert with each other from the viewpoint of reduction of silver ions by gelatin, insofar as the electrochemical potential of a solution should correspond to the Fermi level of a solid.[8]

The reducing property of gelatin has been noted and studied for many years.[3,4,8,10–24] It was also described in the literature that silver clusters may be formed on silver halide grains during the precipitation of the grains as a result of the reduction of silver ions by gelatin,[13,14,16,18,21,23] and that sensitivity increased with increasing pH value of the reaction medium during the precipitation processes.[16,18] Szucs proposed that the reducing ability of gelatin arose from methionine and sugar

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Original manuscript received March 12, 2002

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content.[16,18] Using an analytical method, Kobayashi et al. ascribed the reducing property of gelatin to some kind of sugar, which was bound by gelatin.[12] Urabe and Sano characterized the reducing property of gelatin by comparing its performance with that of a synthetic polymer.[23] Pouradier summarized the redox properties of gelatin and the roles of gelatin on silver cluster formation during the precipitation of silver halide grains, and pointed out that gelatin could stabilize nascent silver clusters.[14] However, no quantitative redox analysis has been made on the silver cluster formation during the precipitation of silver halide grains in emulsions.

The present study was undertaken to observe and quantitatively examine the formation of silver clusters during the precipitation of silver halide grains in emulsions in terms of the difference between E_{Ag} and E_{Gel} in the reaction solutions. The values of E_{Gel} in the reaction solutions were varied by changing their pH values. The formation of silver clusters was detected indirectly, by observing the increase in sensitivity caused thereby. An interpretation from the electrochemical viewpoint is applied to the process of the silver cluster formation during the precipitation of silver halide grains in this study, and related to the processes of silver cluster formation taking place during the digestion of liquid emulsions[3] and storage of dried emulsion layers.[4]

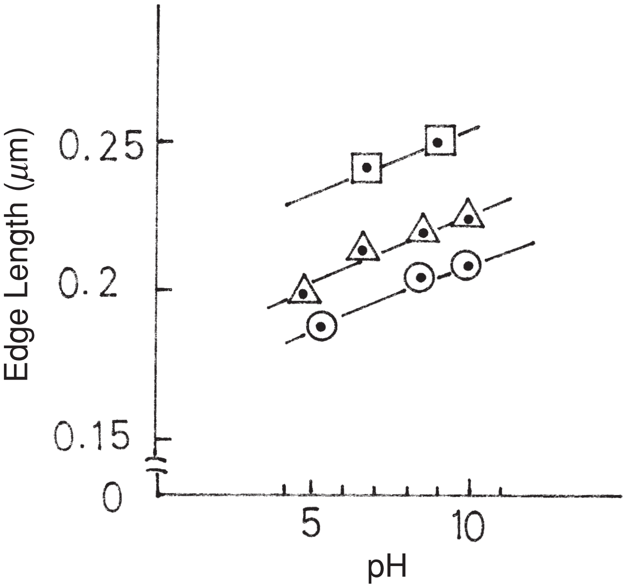

Figure 1. Average edge lengths of silver bromide grains, which were precipitated at 75°C by a controlled double jet method with pH values indicated on the abscissa and E_{Ag} values of 50 mV (O), 100 mV(Δ), and 150 mV(□).

Materials and Experiments

Photographic emulsions composed of fine AgBr grains and deionized gelatin were prepared by a controlled double jet method,[25] according to which aqueous solutions of 1N $AgNO_3$ and 1N KBr are simultaneously poured into an aqueous gelatin solution at 75°C over 41 min. The pAg and pH values of the bulk reaction medium was kept constant during the precipitation of AgBr grains. The pAg values were adjusted to +50 mV, +100 mV, and +150 mV versus SCE at 75°C, and the pH values were adjusted in the range from 4 through 10 at 75°C. Subsequently the resulting emulsions were subjected to the flocculation to eliminate most of the KNO_3. We then added gelatin, and adjusted pH and pAg values to 6.5 and 8.3 at 45°C, respectively, in order to make it available as an photographic emulsion. The sizes of the resulting grains were measured from electron micrographs of the carbon replicas of the grains taken with an electron microscope Model JEM-1010 (JEOL, Tokyo, Japan).

Layers of the emulsions were prepared by coating and drying them on cellulose triacetate film base, and subjected to sensitometric measurement. According to circumstances, hydrogen hypersensitization was applied to the emulsion layers by evacuating them for 1 hr and then putting them under hydrogen gas at atmospheric pressure and room temperature for 3 hrs. The emulsion layers were exposed to a tungsten lamp of color temperature of 2856K for 10 sec through a continuous wedge. Exposed emulsion layers were developed using MAA-1 developer[26] at 20°C for 10 min. According to circumstances, emulsion coatings were subjected to gold latensification prior to development in order to detect undevelopable silver clusters on the grain surface, using a solution prescribed by James et al[27] at 20°C for 3 min, and washed for 30 min.

The E_{Ag} value was measured for a stirred reaction solution by use of a silver electrode as a working electrode and an Ag/AgCl electrode as a reference electrode. The E_{Gel} value was measured at 75°C for a stirred aqueous solution (3 wt %) of a deionized gelatin (Rousselot 52383) by use of a platinum electrode as a working electrode and an Ag/AgCl electrode as a reference electrode, and assigned the value recorded 3 min after the platinum electrode was immersed in the gelatin solution, since we observed that E_{Gel} changed slighty with time. The measured values of both E_{Ag} and E_{Gel} are expressed with respect to the sarurated calomel electrode (SCE).

Results

According to the procedure described in the previous section, cubic AgBr grains, average edge lengths of which were shown in Fig. 1, were formed with variation of the pH and pAg values of the bulk reaction medium during the precipitation process. It was observed that the average edge length of the grains increased with the increase in the pH values and the increase in the E_{Ag} values, i.e., the decrease in the pAg values, of the bulk reaction solution.

Relative sensitivity and fog density of the layers of these emulsions are shown in Fig. 2 as a function of the pH and pAg values of the bulk reaction medium during the precipitation process. As seen in this figure, all the emulsion layers were free from fog. Since the intrinsic sensitivities of emulsion layers are generally proportional to the average volumes of the grains in the emulsions,[1,28] the observed sensitivities of the emulsion layers were divided by the average volumes of the corresponding emulsion grains and used in Fig. 2. As seen in this figure, the sensitivities of the emulsions increased with increasing the pH values of the bulk reaction medium during the precipitation process, while they were nearly independent of the pAg values. The degree of the increase in the sensitivity due to the increase in the pH values was as large as two orders of magnitude, and comparable to that of the sensitivity increase caused by reduction sensitization for cubic AgBr grains with similar size reported in a former paper in this series.[3] We note that none of these emulsion layers exhibited any internal sensitivity.

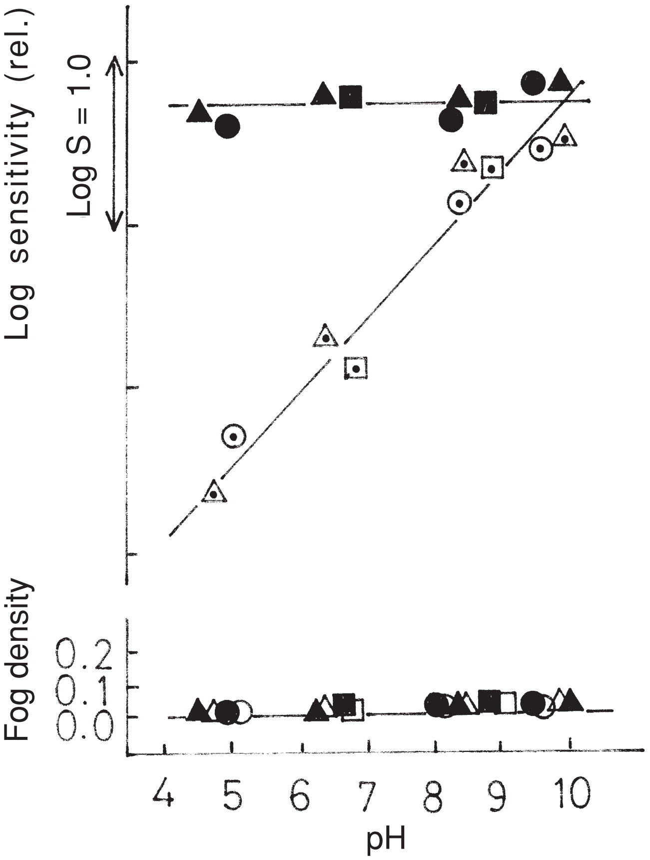

Figure 2. Photographic sensitivities and fog densities of unsensitized (U) (O, Δ, and □) and hydrogen hypersensitized (H_2) (●, ▲, and ■) cubic silver bromide grains with edge length of 0.2 μm, which were precipitated with E_{Ag} values of 50 mV(O, ●), 100 mV(Δ, ▲), and 150 mV(□,■) and pH values indicated on the abscissa.

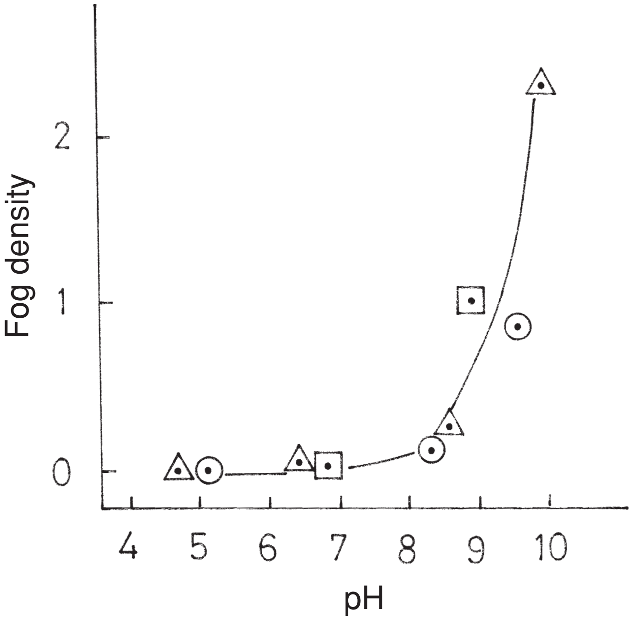

Figure 3. Fog densities of gold-latensified cubic silver bromide grains with edge length of 0.2 μm, which were precipitated with E_{Ag} values of 50 mV(O), 100 mV(△), and 150 mV(□) and pH values indicated on the abscissa.

The emulsion layers were then subjected to hydrogen hypersensitization prior to sensitometric measurements, and the observed sensitivities and fog densities are also shown in Fig. 2. As seen in Fig. 2, all the hydrogen hypersensitized emulsions were free from fog. By hydrogen hypersensitization, the sensitivities were raised and became independent of the pH values during precipitation. We note that the sensitivities of the hydrogen hypersensitized emulsions are nearly equal to those of the layers of the emulsions which were prepared in the reaction solutions with the highest pH value, i.e., 10, under the present experimental conditions.

The layers of the emulsions characterized in Figs. 1 and 2 were subjected to gold latensification and development. Figure 3 shows the fog densities of the gold-latensified emulsion layers as functions of the pH and pAg values of the bulk reaction medium during the precipitation process. As seen in this figure, the fog densities hardly increased in the lower pH region and then steeply increased in the higher pH region with increasing the pH values, while they remained independent of the pAg values.

Discussion

As seen in Fig. 1, the average edge lengths of the grains decreased with decreasing E_{Ag} and also with decreasing pH of the bulk reaction medium during their precipitation process. The observed E_{Ag} dependence of the grain size was understandable in light of the facts that the growth of silver halide grains is usually depressed by decreased solubility of the grains, and that the solubility of AgBr grains decreases with decreasing E_{Ag} under the present experimental condition.[29,30] The observed pH dependence of the grain size was understandable in the light of the following considerations. Namely, AgBr grains were negatively charged and preferably adsorbed positively charged species under our experimental conditions.[31,32] Since the reduction in the pH value of an aqueous solution should ionize functional groups of gelatin and make them positively charged, it should enhance the adsorption of gelatin to the grains, resulting in inhibition of the growth of the grains by the gelatin.

The results described in the previous section have led us to the idea that the enhancement of the sensitivity was achieved by increasing the pH values of the reaction solutions during the precipitation processes to cause formation of reduction sensitization centers owing to the reduction of silver ions by gelatin. This idea was supported by the facts that the sensitivity of an AgBr emulsion was increased, up to the level of sensitivity of the hydrogen hypersensitized ones by increasing the pH value of the reaction medium during precipitation, and that the sensitivity of the emulsion, when enhanced by hydrogen hypersensitization became independent of the pH value during precipitation. It is known that Ag_2O may be formed in an aqueous solution with high pH value. However, it seemed unlikely that Ag_2O formed in under our reaction conditions since the reaction solution contained a high concentration of bromide ions, which should combine with silver ions to form AgBr, with much lower solubility than that of Ag_2O.

The processes, electrochemical expression, and rate of the silver cluster formation due to the reduction of

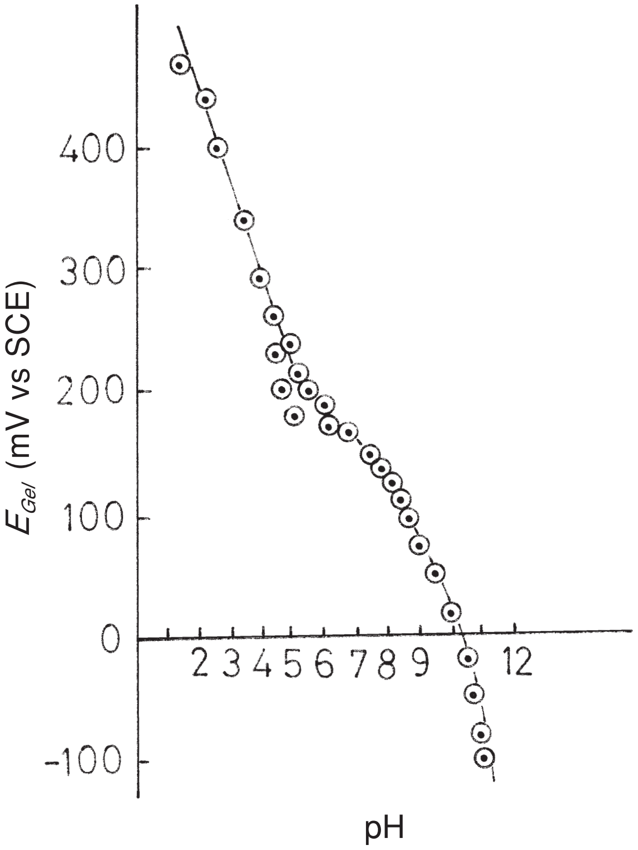

Figure 4. Values of E_{gel} of aqueous gelatin solutions (3 wt %) as a function of pH.

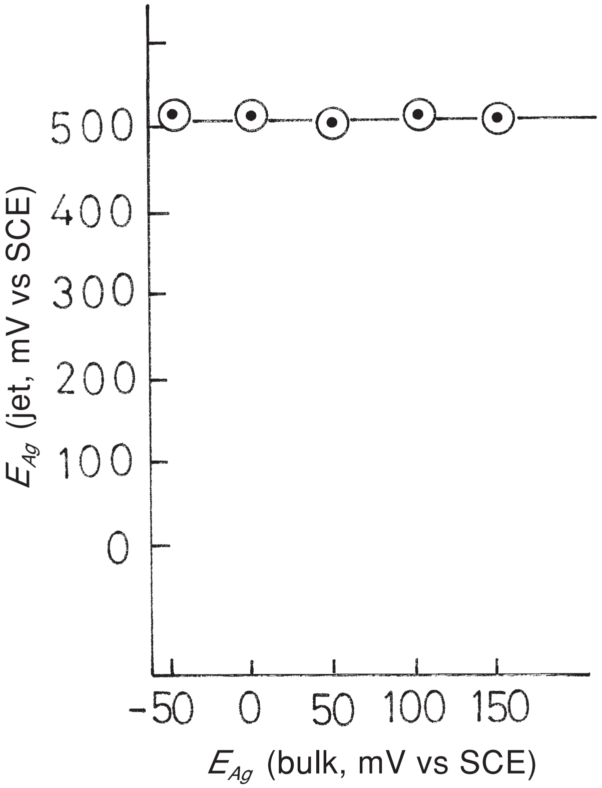

Figure 5. Values of E_{Ag} in the region into which an aqueous solution of 1N silver nitrate was introduced as a function of E_{Ag} values of the bulk of the reaction medium for the precipitation of silver bromide grains.

silver ions by gelatin have been described in Eqs. (1) through (5). It is noted that the silver cluster formation due to the reduction of silver ions by gelatin should take place when the value of ΔE was positive, and that its rate should be enhanced by increasing the value of ΔE. However, the sensitivities of AgBr grains as shown in Fig. 2 were independent of the E_{Ag} value of the bulk reaction solution under the present experimental conditions. This result does not seem to be consistent with Eq. (5), and makes it necessary to quantitatively examine the reduction of silver ions by gelatin during the precipitation of AgBr grains in the light of Eq. (5).

The E_{Gel} value of aqueous gelatin solutions under the condition corresponding to the emulsions in Figs. 1 and 2 was measured as a function of pH, as shown in Fig. 4. As shown in this figure, E_{Gel} of an aqueous gelatin solution sharply decreased with increasing pH. When the E_{Ag} values of the reaction solutions were 50, 100, and 150 mV, as employed in the experiments in this study, the pH values of aqueous gelatin solutions with ΔE of zero, which should be the thresholds for the reduction of silver ions by gelatin, were ~9.5, ~8.5, and ~7.5, respectively. As seen in Fig. 2, the reduction of silver ions by gelatin to form silver clusters took place at pH values below these thresholds, their rates being independent of the silver potential of the bulk reaction solutions.

Then, the E_{Ag} value in the region in the reaction solution, into which an aqueous solution of 1N $AgNO_3$ was introduced, was measured and plotted against the E_{Ag} value of the bulk reaction solutions in Fig. 5. As seen in this figure, the former was nearly 500 mV, independent of the E_{Ag} value of the bulk reaction solution. Then, the value of ΔE in the region where an aqueous solution of 1N $AgNO_3$ was introduced in the reaction solution was estimated by putting the E_{Gel} values (Fig. 4) and the E_{Ag} values (Fig. 5) into Eq. (4), and the results are plotted against the corresponding pH values in Fig. 6. As seen in this figure, the value of ΔE is invariably positive, independent of the E_{Ag} value of the bulk reaction medium, and increases with increasing the pH value. We therefore predict from these data that silver cluster formation should take place at any pH value described in Fig. 6, and that its rate should increase with increasing pH value. This prediction was in good accord with the observations shown in Fig. 2. We therefore propose that the silver cluster formation takes place, not in the bulk of the reaction solution, but in the region into which the aqueous solution of 1N $AgNO_3$ is introduced, and that the resulting clusters became reduction sensitization centers.

In comparison, Fig. 7 shows the sensitivities and fog densities of reduction sensitized cubic AgBr emulsion layers with average size of 0.2 µm without and with gold latensification treatment as functions of the amount of dimethylamine borane complex (DMAB) used for the reduction sensitization. With increasing amount of DMAB, the sensitivity increased through two steps; then the fog density began to increase. It is known that the first and second steps of the sensitivity increase are caused by formation of R and P centers of reduction sensitization,[2,6] respectively; R and P centers act as traps for

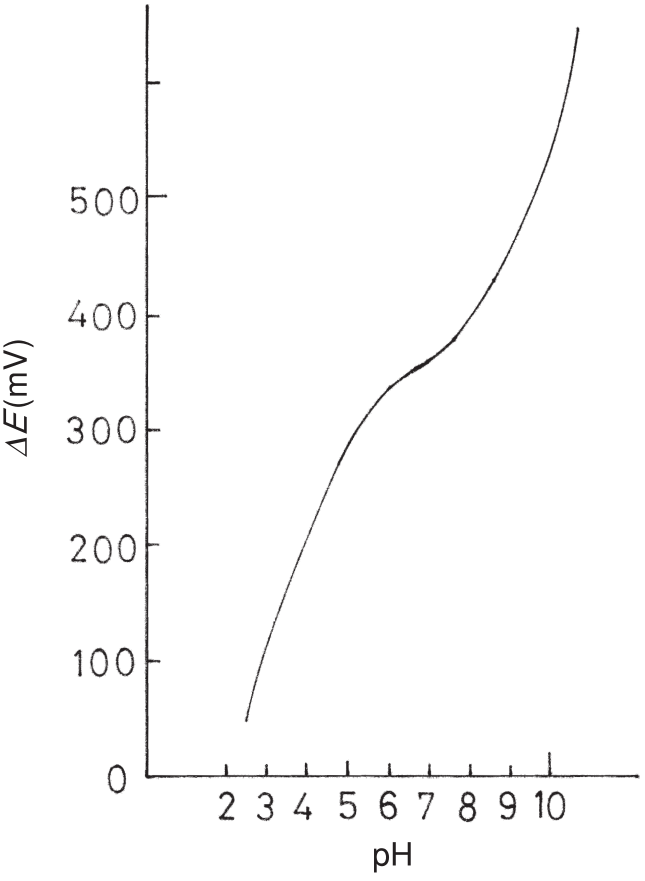

Figure 6. Value of ΔE in Eq. (4) in the region into which an aqueous solution of 1N silver nitrate was introduced as a function of pH values of the bulk reaction medium for the precipitation of silver bromide grains.

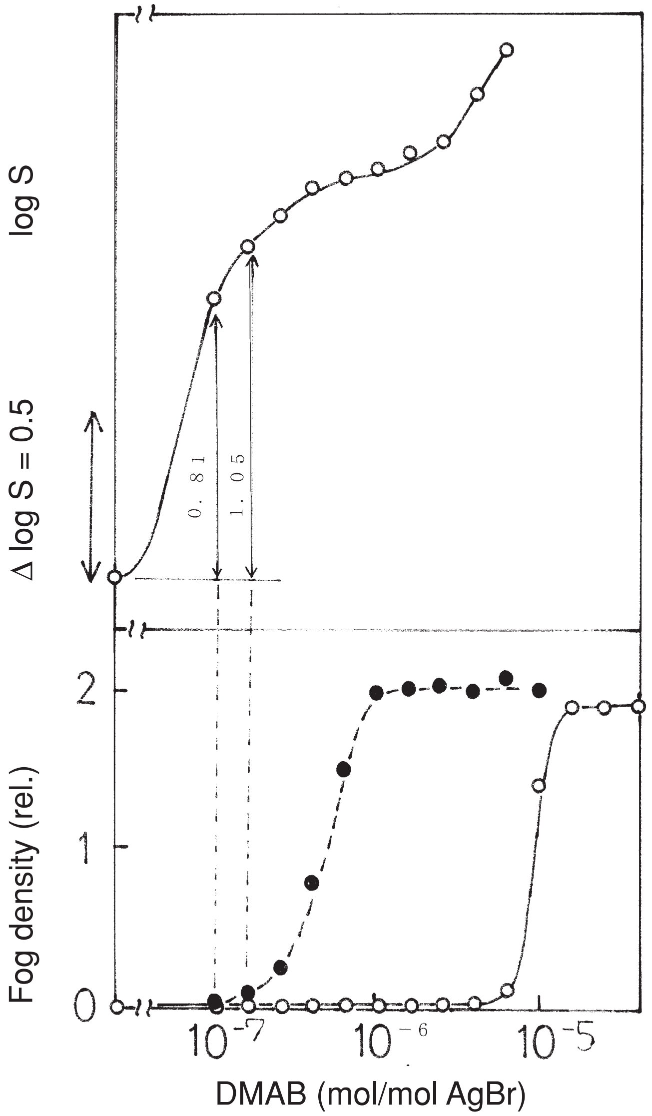

Figure 7. Sensitivities and fog densities of untreated (**O**) and gold-latensified (●) cubic silver bromide grains with edge length of 0.2 μm in emulsions which were digested at 60°C for 60 min for reduction sensitization in the presence of DMAB, amounts indicated on the abscissa.

positive holes and photoelectrons, respectively. Gold latensification renders P centers developable, while it hardly renders R centers developable at all. From the comparison among Figs. 2, 3, and 7, we infer that the concentration of reduction sensitization centers increases with increasing pH value of the reaction medium, and that formation of R centers precedes the formation of P centers. As seen in Fig. 7, the increase in sensitivity with increasing pH value in the lower pH region in Fig. 2 was hardly associated with any increase in fog density on gold latensification in Fig. 7. On the other hand, the increase in sensitivity with increasing pH value in the higher pH region was associated with significant increase in fog density after gold latensification. We therefore propose that the increases in sensitivity in the lower and higher pH regions were mainly ascribed to the formation of R and P reduction sensitization centers, respectively.

Phenomena resulting from silver cluster formation due to the reduction of silver ions by gelatin were observed during precipitation of AgBr grains in liquid emulsions in this study, during digestion of liquid AgBr emulsions and during storage of dried AgBr emulsion layers in the former papers. The phenomena resulting from reduction of silver ions by gelatin were observed in the cases of precipitation and digestion when values of ΔE in Eq. (4) were positive, as observed in the case of storage of a dried emulsion layers under the condition that the Fermi level of a gelatin layer was higher than that of silver. All these phenomena may be unified, insofar as the electrochemical potential of a solution should corresponds to Fermi level of a solid.[9]

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