Unveiling the Composition of Sulfur Sensitization Specks by their Interaction with TAI

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A two-step process for the formation of sensitivity centers different from earlier described two-step processes was found for sulfur sensitized emulsions. After deposition of sulfur in the first step, it was found that the second step does not consist of rearrangement of sulfur over the surface, but of the supply of silver interstitial ions towards the deposited sulfur clusters. The two processes could be separated by adsorbing and desorbing TAI (4-hydroxy-1, 3,3a, 7-tetraazaindene) at/from the silver halide surface. When 1.5 mmol TAI/mol Ag is added before the sulfur reaction, the silver interstitials are immobilized but sulfur still can be deposited at the same level. By lowering the pH to 2.50 after this sulfur reaction, TAI is desorbed from the surface and the released interstitials then cause a restoration of the properties of a sulfur system without TAI. These effects could be demonstrated via diffuse reflectance spectroscopy (DRS), sensitometry and dielectric loss measurements. We could also confirm the isolation of silver sulfide clusters by TAI from other chemicals in the solution, by adsorption of TAI on the clusters.

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Introduction

Although sulfur sensitization has been used for a long time in the photographic industry, the exact nature and composition of silver sulfide formed during sulfur sensitization still remain subject of discussion. However, it is generally accepted that sulfur sensitization results in the formation of silver sulfide specks, where sulfide is epitaxially deposited as islands of monolayers on the AgX surface.^{1,2} A quantitative study of this sulfide deposition, in the concentration region of optimum sensitivity, became only possible by studying the reaction with sensitizers containing radioactive sulfur³ (³⁵S). From these tracer experiments it was found that the activation energy of the deposition of sulfur is dependent on the type of sensitizer, while the changes in sensitivity are not,⁴ indicating that the sensitivity centers are formed in a two-step mechanism. Cash proposed that the first step, i.e., the formation of Ag₂S molecules on the AgX surface, is followed in a second step by their rearrangement into larger specks.^{5,6} This means that the sulfur molecules should have a certain mobility over the crystal surface.^{7,8} By studying the properties and structure of the formed silver sulfide clusters via luminescence modulation spectroscopy⁹ and by analysing the size distribution via Smoluchowski's equation¹⁰ it was recently concluded that sensitization centers could consist of clusters no larger than dimers of silver sulfide. The negative charge of the deposited (AgS-) entities can

be compensated by the presence of different numbers of silver interstitials. $^{11}\,$

$$(AgS^{-})_{2} - (Ag_{i}^{+})_{n}$$
 where $n = 0, 1, 2$ (1)

By sulfur sensitizing emulsions in the presence of uniformly distributed Na₂S, again a two-step mechanism was revealed, where sensitization created first positive hole traps and later on electron traps.¹² At low concentrations of Na₂S hole trapping centers were formed, while higher concentrations produce electron traps. From these experiments Tani posed that in a first step monomers are formed, which are hole traps, while in a second aggregation step dimers are formed, which act as electron traps.

In our new approach on sulfur sensitization¹³ the first step is the epitaxial deposition of sulfur ions on the silver halide microcrystal (111) surface to form structures consisting of lattice surface cells with at least one sulfur ion. These deposited sulfur ions, however, are supposed to be immobilized on the surface.¹⁴ In the second step, silver interstitials are attracted towards the deposited sulfur ions, due to the extra negative charge on the sulfur atom. The number of interstitials and their positions towards each other in the formed clusters will determine the properties of the latter as sensitivity centers. Under normal conditions the deposition of sulfur is immediately followed by the supply of interstitials, but in the present work we have tried to separate the two processes by using TAI as a 'chemical knife'. Via diffuse reflectance spectra the presence or absence of interstitials inside the silver sulfide clusters could be monitored.

By addition of TAI to an emulsion, the interstitials inside the AgX crystal are immobilized, so that only the deposition of sulfur takes place and can be monitored

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(step 1). By desorption of TAI from the crystal surface (by lowering the pH), the interstitials are released so they can migrate towards the sulfur atoms (step 2). The effect of TAI on the interstitial concentration has already been known for a long time, but its influence on the properties of the sulfide cluster and on the photographic behavior was commonly interpreted as size and concentration limitation of the clusters.^{15,16} Recently Shapiro¹⁷ provided information about the properties of Ag₂S and (Ag, Au)₂S clusters by adsorption of organic substances, in particular TAI. He called this technique of investigating silver sulfide and silver-gold sulfide centers via adsorbing compounds on these centers 'chemical microscopy', because it provides information about microscopic impurity centers on the silver halide surface.

Experimental

AgBr octahedral microcrystals of 0.4 µm (mean edge length) were prepared by the controlled double-jet method and suspended in aqueous gelatin. The emulsion was diluted until a concentration of 0.883 mol Ag/ kg of emulsion was reached. The pH and pAg of the emulsion were adjusted for each reaction vessel at a total weight of 130 g. The emulsion was further diluted to a total weight of 150 g minus addenda. The concentration of gelatin was 0.5 g/g AgNO₃. In order to form the silver sulfide clusters on the surface, thiosulfate or diacetyl thiourea was added to the emulsion and the temperature was raised. At different time intervals 1.75 mL of the emulsion was taken and coated on a glass plate of 3 \times 3 cm² pre-coated with a gelatin layer of 1 μ m containing hardeners. Under these conditions the infinite thickness is reached for both tracer and DRS measurements.

Diffuse reflectance spectra (DRS) of the coated emulsions were measured after drying overnight. The coated layers (circa 250 µm thick) were placed against the integrating sphere of a SHIMADZU UV-3101-PC spectrophotometer using the white stone spectralon (from Optilas) as a reference. In this configuration the background for unsensitized emulsions was equal to 0.0135 \pm 0.0002 in absorption units, in the wavelength region of 500 nm – 900 nm. Due to the low absorption of the AgX crystal in this region and the low scattering of the silver sulfide clusters, the obtained spectra may be converted from reflectance (R_{∞}) to Kubelka–Munk (KM) values:¹⁸

$$KM = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} \tag{2}$$

Because this KM spectrum is linearly proportional to the concentration,¹⁹ subtraction of the unsensitized emulsion from the sensitized emulsion results in a new KM spectrum, which is proportional to the concentration of silver sulfide only.²⁰ Independent on the concentration of sulfur, the reaction conditions and the morphology of the silver halide grains, all of the obtained spectra could be deconvoluted with a minimum of three Gaussian curves with a maximum at 2.46 eV (505 nm), 2.20 eV (560 nm) and 2.00 eV (620 nm) and with constant width at half peak height. Because finite energy levels are statistically distributed around a mean energy level, the KM values versus wavelength are converted into KM values versus energy. An example of a deconvoluted KM spectrum is represented in Fig. 1. At wavelengths below 500 nm (energies above 2.48 eV) the absorption of the silver bromide matrix increases dras-



Figure 1. Deconvolution of a KM spectrum of an emulsion of sulfur sensitized octahedral crystal into 3 Gaussian bands at 2.47 eV, 2.24 eV and 2.00 eV [500 nm, 550 nm and 620 nm] (6 S, 75°C, 90 min, $E_{Ag} = 84$ mV, pH = 5.60).

tically, so no reproducible signals can be obtained in this region and KM conversion is not valid any more. Note that the different energies found after deconvolution are in excellent agreement with the energy transitions observed by Ehrlich^{21,22} via transient absorption spectra (2.47 eV, 2.21 eV and 1.99 eV). In our view however, these levels correspond with different sizes of clusters, where small clusters absorb at high energy and larger clusters at lower energies.¹³ Further in this article all mentioned KM values at a specific wavelength are the peak values obtained via deconvolution of the spectra.

The number of sulfur atoms that reacted on the surface and formed silver sulfide clusters was measured via tracer analysis. We used outer-labelled ³⁵S thiosulfate and the ripening of the emulsion was identical to non-labelled thiosulfate. After the sulfur reaction the emulsion was coated on glass plates as described above, and washed 3 times with a 0.12 M KBr solution for 1.5 h to remove the unreacted thiosulfate. The emulsion was then dried and the beta activity measured with a proportional counter (Canberra 2404 alpha/beta counter) and compared to the unwashed emulsion. Corrections were made for background radiation and wash efficiencies. The concentration of gold ions incorporated in the emulsion was also measured via tracer analysis (198Au beta activity). The difference in procedure compared to the sulfur tracer analysis is that the emulsion is now washed with a mixture of a Na₂SO₃ (0.01 M) and alanine (0.01 M) solution. The detection limit depends on the specific activity of the radioactive tracer and attains 6E-8 mol and 2E-8 mol/mol Ag for S and Au respectively in optimal conditions.

When adding TAI prior to the sulfur reaction the emulsion is kept at 40°C for 30 min. Because this addition always results in a raise of the pAg value a small quantity of an AgNO₃ solution is added to the emulsion until the original pAg value is reached. The emulsion is then stirred for another 30 min at 40°C; thereafter sulfur is added and the temperature is raised. Concentrations of sulfur are expressed as "S" where x S = x mgNa₂S₂O₃.5H₂O/mol Ag and of gold as "Au" where x Au =x mg KAuCl₄/mol Ag (under our conditions 0.132 mol Ag/150 g emulsion).

Results and Discussion

Adsorption of TAI (4-hydroxy-1,3,3a,7-tetraazaindene) on the crystal surface is well described in literature.²³⁻²⁷



Figure 2. Electrochemical potential and dielectric loss frequency for different concentrations of TAI (60 °C, E_{Ag} = 84 mV, pH = 5.60).

Reaction of TAI with silver ions obeys the following equations:

TAI in solution: TAI-H \leq TAI⁻ + H⁺ pKa = 6.4 (3)

$$TAI^{-} + Ag^{+} \ll TAI - Ag \qquad (4a)$$

TAI adsorbed on the crystal: TAI⁻ + Ag_i^+ <=> TAI–Ag_i^- (4b)

Where TAI is the general name for the compound, TAIis the anionic form of TAI and TAIH is the uncharged form. The effect of TAI on the photophysical and chemical properties of the emulsion is strongly dependent on the quantity of TAI added to the emulsion.

Complexation of TAI with silver ions in the *solution* (Eq. 4a) can be monitored by measuring the dependence of the electrochemical potential (E_{Ag}) on the TAI concentration. This electrochemical potential is measured using a reference electrode and an ion-selective electrode. As a reference we used an Ingold 3M Ag/AgCl gel electrode and a wire of metallic silver as ion-selective electrode. The measured mV is a potential difference (E_{Ag}) , in the solution, between the Ingold electrode and the silver wire. Using the equation of Nernst, the dependence of the electrochemical potential at 25°C on the free silver concentration can be expressed as:

$$E_{Ag} = E^0_{Ag^+ / Ag^0} + 0.059 \log[Ag^+] - E_{ref}$$

Addition of TAI drastically lowers the free silver concentration (low E_{Ag} value) as seen in Fig. 2.

On the other hand one can also measure the influence of TAI on the concentration of silver interstitials (Eq. 4b) using dielectric loss measurements.²⁸ The log Fmax (log frequency) in the dielectric loss spectrum (which is proportional to the ionic conductivity in the AgX phase) shifts from 6.15 without TAI addition to 3.8 with 4 mmol TAI/ mol Ag present (Fig. 2). This indicates a reduction in ionic conductivity by more than 2 orders of magnitude. The reduction in silver concentration was found to be independent of the amount of sulfur present in the emulsion. From Fig. 2 it is clear that TAI decreases the amount of both silver ions in solution and interstitial silver ions, in accordance with Eqs. 4a and 4b.

When emulsions are chemically sensitized with sulfur the *diffuse reflectance spectra* (DRS) show an increase in absorption from 500 nm until 650 nm (an example of a spectrum of a sulfur-sensitized emulsion



Figure 3. Influence of different TAI concentration—added before sulfur digestion—on the absorption (KM value) at 3 different wavelengths (50 °C, $E_{Ag} = 84$ mV, pH = 5.40, 4 S, 120 min).

is represented in Figs. 1 and 6). Monitoring the growth of the different sizes of silver sulfide clusters with diffuse reflectance spectroscopy was already demonstrated in earlier work.^{20,29} By using dry coatings, however, we could lower the detection limit to 4 E-6 mol S/mol Ag), so we were able to study the sulfur deposition via diffuse reflectance spectroscopy at realistic optimal sensitivity (8 E-6 mol S/mol Ag) of the emulsion. The raise in absorption of the sulfur species starts at 500 nm and with increasing concentration and reaction time bands appear at higher wavelengths (until 650 nm). When the quantity of sulfur reacted on the surface is measured via tracer analysis we find a linear relationship with the KM values of the diffuse reflectance spectrum starting from 1 S.¹⁴ The slope of this curve is different at different wavelengths of absorption. When TAI is added to the emulsion before the sulfur reaction, this relationship is no longer valid. The absorption at different wavelengths in diffuse reflectance spectroscopy thus strongly depends not only on the presence of silver sulfide clusters on the crystal surface but in the first place on the presence of silver interstitials in these clusters.

Figure 3 represents the KM value of emulsions with different concentrations of TAI added before the sulfur reaction. No significant effect is noted below 0.5 mmol TAI/mol Ag but at higher concentrations the absorption values drastically drop at all wavelengths, and are almost zero at 2 mmol TAI/mol Ag. On the other hand addition of 1 mmol TAI/mol Ag *during* and *after* the sulfur reaction results in a stabilization of the DRS spectra (Fig. 4). This stabilization can be explained as follows: TAI is strongly adsorbed at the clusters, in accordance with Shapiro's observations,17 and the interstitials are kept invariably located in the clusters, so the composition of the cluster remains the same and no changes are observed in the KM spectra (see also sulfur - TAI - gold interaction). This effect is paralleled by sensitometric observations, where the increase of sensitivity and fog during sulfur ripening are stopped by the addition of TAI.¹⁶

The addition of TAI to the emulsion and its consequent adsorption on the surface could alter the number of sulfur atoms deposited on the surface. So the same experiment was carried out with labelled thiosulfate. Figure 5 shows that the quantity of sulfur deposited on the surface decreases only gradually from 2 mmol TAI/mol Ag on. In the region where the absorption is almost zero



Figure 4. Influence on DRS of TAI addition (1 mmol / mol Ag) at different reaction times of thiosulfate (560 nm, 60 °C, pH = 5.60, $E_{Ag} = 84 \text{ mV}$, 6 S, 1 mmol TAI / mol Ag).



Figure 5. Influence of the TAI concentration on the uptake of sulfur ions (50 °C, E_{Ag} = 84 mV, pH = 5.40, 2 S, 120 min).

(Fig. 3) the sulfur uptake remains rather constant, in accordance with former observations,¹⁶ indicating that the use of TAI below 2 mmol/mole Ag does not affect the quantity of sulfur deposited.

For further experiments we will use TAI concentrations of 1.5 E-3 mol TAI/mol Ag and lower, where changes in spectra are only due to variations in silver interstitial concentration and not to changes in the sulfide concentration on the surface. It is important to notice that the activation energy of the sulfur reaction was calculated from data obtained by tracer analysis and found to be (0.97 ± 0.08) eV both in the absence and in the presence of TAI (1 E-3 mol TAI/mol Ag).

Desorption of TAI

From Eq. 3 it is clear that by changing the pH one can change the equilibrium concentration of protonated TAI and deprotonated TAI. This should result in a change in adsorption of TAI on the crystal surface and consequently alter the concentration of free silver interstitials (Eq. 4b). The effect of this release process of silver interstitials on the properties of silver sulfide clusters is studied with different measuring techniques.

When TAI is added one hour before the sulfur reaction most interstitials are immobilized. The concentra-



Figure 6. DRS spectrum of desorption of TAI (1 E-3 mol/mol Ag) by lowering pH; 1) 50°C, pH = 2.50, 180 min; 2) 75°C, pH = 2.50, 180 min.

tion of silver ions in solution is restored by adding $AgNO_3$; thiosulfate is added to the emulsion and the temperature is raised between 60 to 75°C. After 1.5 - 2 h of reaction most of the sulfur has reacted on the surface (65 – 80%). By lowering the pH after the sulfur reaction is complete, TAI can be desorbed from the surface (Eq. 3), causing an increase of the interstitial concentration (Eq. 4b). An increase of the E_{Ag} value can also be observed due to the release of free silver ions via Eq. 4b; this E_{Ag} change is also corrected for.

DRS

An example of a desorption experiment measured via DRS is shown in Fig. 6. The upper curve shows the spectrum of the sensitized emulsion without TAI. The lowest curve is the one with 1 mmol TAI/mol Ag added before sensitization. Lowering the pH to 2.50 at high temperature after the digestion results in a spectrum which is identical to the pure sulfur-sensitized emulsion at pH 5.50. From tracer experiments we find that for all curves of the figure the sulfur turnover is the same (67.5 ± 7.5) %. So it is clear that the raise in optical adsorption is not due to an increase in sulfur deposition.

This experiment was repeated with diacetylthiourea as sulfur donor, because it is a more labile sulfur compound and causes a faster sulfur deposition and a higher yield (92%). Consequently no extra sulfur deposition is then expected during the desorption step. For this experiment the optical effect was exactly the same. On the other hand lowering the pH of the pure sulfur system (without TAI) after the sulfur reaction neither changes the DRS spectrum nor the sulfur uptake. The fact that the spectrum for desorption is similar to the pure sulfur sensitization indicates that the cluster size distribution on the surface is identical in both cases.

Dielectric Loss

Dielectric loss measurements of desorption experiments are represented in Fig. 7. Curve 1 shows the dielectric loss values for an emulsion with different concentrations of TAI added at pH 5.60. On curve 2 the dielectric loss values are plotted for the same samples except that now the pH is lowered to 2.50 (E_{Ag} is corrected for). Lowering the pH to 2.50 results in a restoration of the original frequency value, which means that the concentration of silver interstitials is reestablished.

When the interstitials are released back into the crystal, by desorption of TAI, they can migrate to the al-



Figure 7. Dielectric loss frequency for desorption of different TAI concentrations (60 °C, E_{Ag} = 84 mV) from pH = 5.6 to pH = 2.5.

ready formed silver sulfide clusters and give the same optical properties as for normal sulfur sensitization. For this process the number of interstitials released back into the crystal is sufficient to fill up the cluster to the 'normal' sulfur-sensitized level. It seems highly improbable that the raise of the absorptions measured by DRS after TAI desorption is caused by the aggregation of sulfur over the crystal surface. Aggregation of sulfur as proposed by Cash^{5,6} would implicate a further increase of absorptions even for normal sulfur sensitization, which is not found neither at prolonged sulfur sensitization, nor at prolonged digestion following TAI desorption. When aggregation is the key feature of sensitization, then it should, therefore, come to an end in the course of the process. Furthermore, a continuous increase of gold uptake should be measured. Because gold ions are bonded by two neighboring sulfur ions of the surface lattice (dimers and larger clusters), and not by monomers,^{13,30} prolonged digestion, say aggregation of Ag₂S molecules, should cause increased gold uptake, which however was not found.¹³ The aggregation model can only explain this when aggregation is limited and comes to an end during sensitization, which does not seem obvious.

Different pH Values of TAI Desorption. A quantity of 1.5 E-3 mol TAI per mol Ag was added 60 min before the sulfur reaction at 40°C, and the E_{Ag} was corrected for. After 90 min of reaction with $S_2O_3^{2-}$ at 60°C the pH was lowered to different values. The lower the pH value the more TAI will be desorbed from the surface and the higher the absorption and KM values will be (upper curve of Fig. 8). The concentration of silver interstitials expressed as log frequency of dielectric loss is represented in the same figure (lower curve): the lower the pH of desorption the higher the concentration of Ag_i^+ found. Note that the dielectric loss value in Figs. 7 and 8 are different from those in Figs. 1 and 6 because the E_{Ag} is not corrected for after desorption of TAI. An effect of E_{Ag} correction on an emulsion is only detectable via dielectric loss, not via DRS or tracer analysis.

Temperature Dependence of TAI Desorption. The increase in optical response due to the desorption of TAI and the increase of silver interstitial ions is dependent on the temperature of the solution after the lowering of the pH (Figs. 6 and 8). The reaction was carried out at 60°C, $E_{Ag} = 96$ mV and pH = 5.50; after 90 min of reaction the pH was lowered to 2.50. At high temperature



Figure 8. Desorption of TAI (1.5E-3 mol / mol Ag) at different pH values (60 °C, 180 min, pH=5.50, E_{Ag} = 84 mV, 15 S, 560 nm).



Figure 9. Desorption of TAI (1.5 E-3 mol / mol Ag) at different temperatures (60°C, 180 min, pH=5.50, E_{Ag} = 84 mV, 15 S for log freq. and 4 S for KM, 560 nm).

 $(75^{\circ}C)$ the increase of the absorption value is extremely fast, while at low temperature $(37^{\circ}C)$ it is much slower.* Note that the KM value for a pure sulfur sensitization reaction at these low temperatures is normally much lower, but now sulfur has already been deposited on the surface at $60^{\circ}C$.

On these samples the dielectric loss values were measured (Fig. 9). The log frequency values however are scarcely affected by the temperature of desorption (Fig. 9) and the log frequency values are at a low level, even at the lowest temperature. This means that the interstitials that are sequestered by TAI are released very quickly (without any activation energy) in the crystal. To find their way to the sulfur however they need temperature and activation energy as shown by the DRS (Fig. 9). From these results the activation energy was calculated from the DRS spectra.

^{*} Here the sulfur uptake (thiosulfate) was also significantly higher after the pH drop (63% to 75% at 75°C), part of the increase in this experiment can be due to an increase in sulfur uptake or the formation of S (low pH).



Figure 10. Photographic behavior of an emulsion with and without TAI, desorption at 50°C and 75°C (TAI =1.5 E-3 mol / mol Ag; $E_{Ag} = 84$ mV, 90 min reaction and 90 min desorption, sensitivity measured at 0.5 density above fog).

First the DRS spectra were fitted, i.e., the KM values versus reaction time using the following equation:

$$KM = KM_{sat}(1 - e^{-kt})$$
(5)

The validity of the above equation was established by plotting a straight line of log $(1 - KM/KM_{sat})$ versus time. From the slope of the resulting graph the rate constant could be calculated. The slope of the rate constant (k) at different temperatures then gives us the activation energy. For fast reactions the error on the rate constant can be large since there are no KM values at time intervals shorter than 10 min. For slow reactions on the other hand it is sometimes difficult to determine the saturation for the Kubelka–Munk value.

The activation energy of the pure sulfur sensitization without TAI was calculated from the DRS spectra at 505 nm, 560 nm and 620 nm and found to be equal (0.99 \pm 0.10) eV for sensitization with thiosulfate and with diacetyl thiourea. For the sulfur deposition via thiosulfate we found via tracer analysis under our experimental conditions that the activation energy was $(0.97 \pm$ 0.08) eV while it is much lower for diacetyl thiourea. The fact that the activation energy of sensitization obtained via DRS is nevertheless similar for both sulfur reagents supports the idea that we don't observe pure sulfur entities in diffuse reflectance; the supply of interstitials is essential. The rate-determining step in sulfur sensitization appears to be not the sulfur deposition but the supply of interstitials to the deposited sulfur.

The activation energy for the desorption experiment was also calculated from the KM value and found to be ca. 0.25 eV. This is the energy needed to supply the interstitials to the formed silver sulfide clusters (energy for diffusion) while a substantial amount of interstitials still has to be formed (activation energy for interstitial formation).⁵

Effect of TAI Desorption on the Photographic Behavior. The effect of TAI desorption on the photographic behavior is represented in Fig. 10. Again there is a major difference between addition of TAI before the sulfur sensitization (lowest curve) and pure sulfur sensitization (highest curve). By desorption of TAI one can restore the photographic behavior to the pure sulfur

TABLE I. Uptake of Gold lons for Different Concentrations of Gold and TAI in the Absence of Deposited Sulfide

% of gold uptake	5.4 E-6 mol Au	1.6 E-5 mol Au
0.5 E-3 mol TAI	(-0.8 ± 1.3) %	(1.3 ± 1.3) %
1.5 E-3 mol TAI (pH 5.6)	(15 ± 2) %	(33 ± 3) %
1.5 E-3 mol TAI (pH 2.5)	(23 ± 3) %	(42 ± 4) %



Figure 11. Sulfur reaction (60 min) followed by a) upper curve: addition of TAI (60 min) and gold (60 min); b) lower curve: addition of gold (60 min) and TAI (60 min) [6S, pH = 5.60, 84mV, 560 nm].

sensitized emulsion. A similar effect was observed for the absorptions in Fig. 6.

From these TAI desorption experiments we can conclude that ripening can occur again due to released interstitials. It seems more probable that these interstitials play the key role in sulfur sensitization of the emulsion, rather than aggregation of sulfur, and also that they are responsible for the appearance of absorption bands in DRS during sulfur sensitization.

Interactions between Sulfur, Gold and TAI

In earlier work it was already mentioned that gold ions will only be incorporated in silver sulfide clusters composed of at least 2 sulfur atoms.^{13,28,30} From the uptake of gold ions one can thus get an idea about the cluster size distribution. The level of gold uptake can be used to verify if TAI adsorbed on the silver sulfide clusters possibly prohibits any reaction between gold and sulfide ions. The ideal way to study this is by using radioactive gold ions. We noticed however that even without sulfur present a large fraction of gold is not removable from the emulsion, depending on the TAI and gold concentration (Table I).

By lowering the pH to 2.50, more TAI is present in solution and an even higher amount of gold ions cannot be removed by washing. Apparently, part of the gold ions strongly interacts with TAI to form a compound which is not removable, at least not by Na₂SO₃ and KBr washing. Tracer analysis with ¹⁹⁸Au and the study of incorporation of Au in silver sulfide clusters thus appear to be impossible in the presence of TAI. Note however that this conclusion is only valid when using HAuCl₄ as a gold donor. The uptake of gold in the presence of TAI can apparently be measured when using gold thiocyanate complexes as donor,¹⁶ probably due to the destabilisation of the gold-TAI complex.

The absorption bands in diffuse reflectance, however, are strongly suppressed by gold present in the silver sulfide clusters due to the absence of interstitials.¹³ On the lower curve of Fig. 11 one can see that by adding

gold after sulfur sensitization the intensity of the absorption band at 560 nm has almost completely vanished. Addition of TAI after this gold ripening results again in a small increase of the absorption, which may be due to the removal of some gold out of the clusters. The same experiment was repeated, but before the addition of gold TAI was added to the emulsion. As can be seen on the upper curves of Fig. 11, the addition of TAI doesn't influence the KM value at 560 nm. Addition of gold afterwards gives only a slight decrease in absorption. These effects can also be observed at other wavelengths of absorption. From DRS measurements one can thus conclude that TAI prohibits the uptake of gold ions in silver sulfide clusters. This is also in accordance with (and confirms) earlier photographic observations.16

Conclusion

It was found that the formation of silver sulfide sensitivity centers occurs according to a two-step process. First there is the deposition of sulfur on the silver halide surface as epitaxial structures at positive kink sites. This deposition reaction is independent on the presence of interstitial silver ions but dependent on the sulfur donor added. The deposited sulfur entities carry a partial negative charge, so in a second step silver interstitials migrate towards these sulfide structures. By the presence of these silver interstitials inside the clusters the charge of the clusters becomes partially positive, so upon illumination they function as electron traps. This second step is independent on the sulfur donor added, and has an activation energy of (0.25 \pm 0.10) eV. It is this second reaction which gives rise to the absorption spectrum. The two different steps could be studied independently from each other by adding TAI to the emulsion. By doing so the silver interstitials are immobilised, so that sulfide clusters can be formed on the silver halide surface, which have a deficiency of Ag_{i+}^{+} , and have optical and photographic properties different from 'normal silver sulfide clusters'. When the interstitials are released again into the crystal, by desorption of TAI, they fill the silver sulfide clusters to the 'normal' state of the pure sulfur sensitized emulsion and provide the same properties as those of pure silver sulfide clusters.

When TAI is added after the sulfur the properties of the clusters are not altered since the interstitials are already present in the sulfide cluster. This TAI addition after the sulfur reaction however prohibits gold ions from reacting with the formed silver sulfide clusters, indicating:

that TAI is strongly adsorbed at the sulfide clusters most probably because of the interstitials present in them

• that TAI in this way isolates the clusters and prevents or retards reaction with the aqueous environment

Not only from DRS but also from photographic behavior we can conclude that the key role in the functioning of silver sulfide clusters and their composition is played by interstitial silver ions in the formed silver sulfide clusters.

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