

Functioning of Thiocyanate Ions During Sulphur and Sulphur-Plus-Gold Sensitization

E. Charlier, R. Gijbels

*University of Antwerp (UIA), Department of Chemistry
Antwerp, Belgium*

*M. Van Doorselaer, R. De Keyzer
Agfa-Gevaert N.V., R&D Laboratories
Mortsel, Belgium*

Abstract

Not much about the effect of thiocyanate addition on the sulphur ripening is known, although it is used for many applications in photographic practice. Via a combination of tracer analysis and diffuse reflectance spectroscopy the effect of thiocyanate addition on the sulphur and sulphur-plus-gold ripening could be unveiled. When thiocyanate is added prior to the sulphur addition, it appears to rearrange the silver halide surface in such way that the sulphur deposition rate is enhanced, but the supply of interstitials is limited. Addition of thiocyanate after the sulphur reaction results in the formation of thiocyanate complexes with silver, from which a silver ion is more easily deposited in a surface cell of the silver sulphide clusters thus enhancing the sensitization rate.

For sulphur-plus-gold sensitized emulsions it was observed that part of the gold ions could be removed out of the $\text{Ag}_{2-x}\text{Au}_x\text{S}$ clusters by addition of thiocyanate ions and subsequent washing. Hence, it was concluded that two different types of gold ions are present in the silver sulphide clusters;

1. gold ions which are substitutional for silver (bound between sulphur and bromide ions)
2. gold ions which bridge two or three sulphur atoms.

Incorporation of gold ions into silver sulphide clusters suppresses their optical absorption in diffuse reflectance spectroscopy. Since the optical absorption at 505 nm can completely be restored by addition of thiocyanate, it is assumed that the entity absorbing at this wavelength is a monomer of silver sulphide.

Introduction

Recently we introduced a new two-step model for the formation of sensitivity centers on the surface of silver halide microcrystals^{1,2}. In this new approach, the first step consists of the epitaxial deposition of sulphur ions on the silver halide microcrystal (111) surface to form structures

consisting of lattice surface cells with at least one sulphur ion. These deposited sulphur ions are supposed to be immobilized on the surface³. In the second step (formerly thought to consist of aggregation of Ag_2S molecules), silver interstitials are attracted towards the deposited sulphur ions due to the extra negative charge on the sulphur atom. The number of interstitials and their positions towards each other in the formed clusters will determine the properties of the latter as sensitivity centers². Under normal conditions the deposition of sulphur is immediately followed by the supply of interstitials. Via diffuse reflectance spectra the presence or absence of interstitials inside the silver sulphide clusters can be monitored. The effect of thiocyanate on the properties of the sulphur and sulphur-plus-gold sensitized emulsions can now be explained using this model. Van Doorselaer extensively described the effect of thiocyanate on the photographic properties and on sensitization⁴, so the main focus in this paper will be put on the optical properties.

Experimental

In this work AgBr emulsions with octahedral shaped crystals of 0.4 μm (main edge length) were used. They were prepared by controlled double jet method in an aqueous solution of gelatin. Chemical sensitization was accomplished by digesting the emulsion with thiosulphate for the pure sulphur sensitization and with diacetyl thiourea for the sulphur-plus-gold sensitization. By using diacetyl thiourea, the catalyzed deposition of sulphur by gold ions is prohibited^{3,5}. The number of gold atoms that reacts with the formed silver sulphide clusters gives crucial information about the cluster size distribution⁵ and was measured via tracer analysis. For these experiments we used $\text{H}^{198}\text{AuCl}_4$ as reagent, where the treatment of the emulsion was identical to the non-labelled gold component. After the reaction, the emulsion was coated on glass plates and washed 3 times with a Na_2SO_3 (0.01 M) and alanine (0.01 M) solution for 18 hours to remove the unreacted gold ions. 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.

Absorption spectra of the sensitized emulsion were obtained by measuring the reflectance of thick layers of the coated emulsion, with reference to unsensitized emulsion, by means of a SHIMADZU UV-3101-PC spectrophotometer. The spectra were deconvoluted at 505 nm, 555 nm and 620 nm^{1,5}. Concentrations of sulphur are expressed as "S" where $x\text{ S} = x\text{ mg Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} / \text{mol Ag}$ and of gold as "Au" where $x\text{ Au} = x\text{ mg KAuCl}_4 / \text{mol Ag}$ (under our conditions 0.88 mol Ag / kg emulsion).

Results and discussion

Addition of thiocyanate to an unsensitized emulsion does not affect the absorption spectra, but results in a change of both the free silver and silver interstitial concentration. The complexation with silver interstitials near the surface is much lower with thiocyanate than with TAI added, but still a large fraction of thiocyanate is present on the surface¹. For all experiments the free silver concentration is restored to its original value by adding small quantities of AgNO_3 . Since the thiocyanate concentration is situated between 0.5 and 10 mmole / mole Ag mainly $\text{Ag}(\text{SCN})_2^-$ is present in solution under our experimental conditions⁶.

1. Influence of thiocyanate on the sulphur ripening

In Figure 1 the influence of different concentrations of thiocyanate on the sulphur uptake via thiosulphate is plotted. In this case thiocyanate is added 60 minutes before the sulphur ripening at a temperature of 40 °C. After 30 minutes the μAg is adjusted to the original value, after another 30 minutes sulphur is added and the temperature is raised to 60 °C. The lowest curve represents the pure sulphur sensitized emulsion (6 S) and the higher curves represent the emulsions where different concentrations of thiocyanate are added. A significant increase in the reaction rate can be observed starting on from 1 mmole / mole Ag added. For lower concentrations of thiocyanate, the differences in reaction rates are not significant. After longer reaction time (2 hours) no difference in the uptake value can be detected, which is in accordance with earlier findings⁴.

When thiocyanate is added prior to the sulphur reaction a decrease in the silver sulphide absorption is observed, depending on the thiocyanate concentration added (Figure 2). Since the same amount of sulphur is deposited after two hours of reaction (see higher) this drop in intensity has to be explained by a change in the silver interstitial concentration. Addition of thiocyanate before the sulphur reaction may cause adsorption of AgSCN and $\text{Ag}(\text{SCN})_2^-$ dipole molecules (positive silver side and negative thiocyanate side) on the surface. These molecules may be adsorbed at the positive kinks of the silver halide surface or, at high concentrations of thiocyanate, bind with its silver ion onto the bromide surface. In this way a new positive kink is formed on the surface, which results in the enhanced deposition rate of sulphur⁵. The negative thiocyanate side,

however, is able to attract the silver interstitials. Since thiocyanate is added prior to the sulphur ripening the attracted interstitials are not available for the silver sulphide clusters. In this way thiocyanate may separate the silver interstitials from the silver sulphide clusters, causing the drop in KM value (as seen in Figure 2). The silver interstitials which are attracted by thiocyanate remain much more mobile than in the case where TAI blocked them¹.

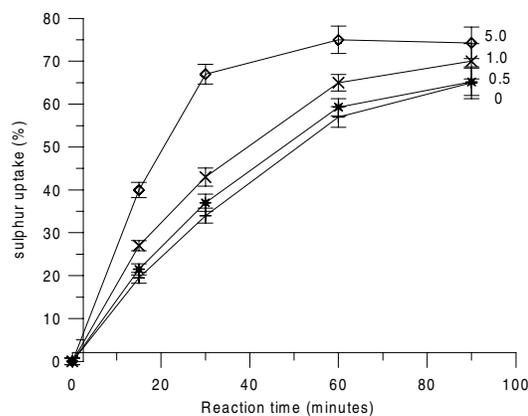


Figure 1. Influence of different concentrations of thiocyanate (mmole / mole Ag) on the sulphur uptake rate (6 S, 60 °C, $\mu\text{Ag} = 84\text{ mV}$, $\text{pH} = 5.60$)

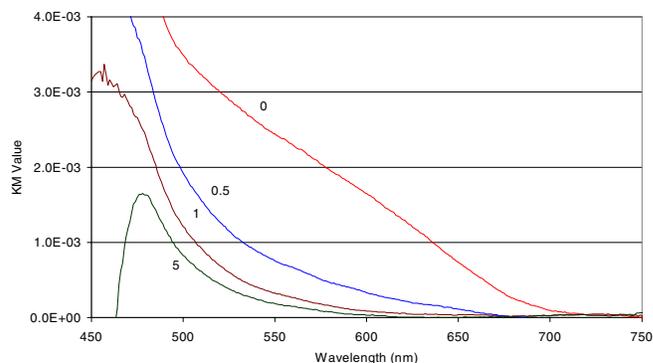


Figure 2. Influence of different concentrations of thiocyanate (mmole $\text{KSCN} / \text{mole Ag}$) added before the sulphur reaction on the KM value

(6 S, 60 °C, $\text{pH} = 5.60$, $\mu\text{Ag} = 84\text{ mV}$, 120 min)

To monitor whether the sulphur atom of thiocyanate takes part in the silver sulphide cluster we used sulphur labelled thiocyanate (K^{35}SCN). By selecting again sulphur-35 as a tracer we could benefit from the optimisations already performed for labelled thiosulphate. Since the adsorption / uptake of SCN^- is identical in the presence and absence of deposited sulphide, one can conclude that thiocyanate is not chemically bonded onto the silver sulphide cluster.

Addition of thiocyanate after the sulphur reaction is completed, on the other hand, does not result in an increase of the sulphur uptake rate measured via tracer analysis. In Figure 3 the Kubelka-Munk value is plotted as a function of wavelength for different thiocyanate concentrations added after the sulphur reaction. Addition of KSCN after the sulphur reaction remarkably results in a decrease of the KM values lower than 600 nm and an increase above 600 nm compared with the pure sulphur sensitized emulsion. As already mentioned in the introduction the spectra of the pure sulphur case can be deconvoluted at the three wavelengths, 505 nm - 560 nm and 620 nm. The curves with thiocyanate added after the reaction, however, can only be deconvoluted with these three wavelengths and corresponding widths at half peak height if one assumes absorption bands at longer wavelengths. All spectra obtained could now be deconvoluted with an extra band at 710 nm (1.75 eV) and a width at half height of 0.28. Again we have to mention that this band could be a combination of more bands, like one at 677 nm (1.83 eV) and 733 nm (1.69 eV), but this could not be consolidated due to the low intensity of the absorptions in this wavelength region. These four wavelengths however, are in excellent agreement with the energy transition found by Ehrlich by studying the transient absorption spectra of sensitized emulsions^{7,8}.

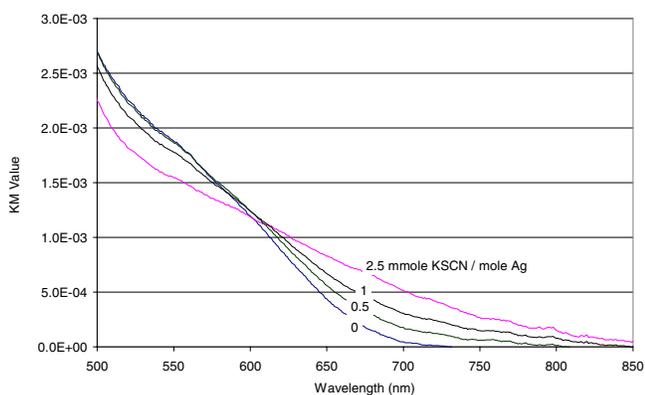


Figure 3. Influence of different concentrations of KSCN added after the sulphur reaction on the KM value (4 S, 60 °C, pH = 5.60, uAg = 84 mV, + KSCN after 2 hours)

This shift in the intensities of the optical absorption bands towards higher wavelengths can be explained by the supply of silver ions towards the silver sulphide clusters. Under normal sensitization conditions the concentration of silver interstitials is lower than the concentration of deposited sulphur². After the complexation of thiocyanate with silver ions, these complexes can be adsorbed on the silver sulphide cluster (via Coulombic interaction) and the silver ion can interact with the silver sulphide clusters. Since this silver ion is supplied via solution it will be located in a surface cell. This silver ion, which bridges two sulphur atoms will be responsible for the transformation from 2 adjacent monomers into one dimer. Due to this supply of interstitials via the solution, higher cluster forms are now detectable via diffuse reflectance spectroscopy. Dimers of

sulphur which have only one interstitial will absorb at 505 nm, but by the supply of silver ions via adsorption of $\text{Ag}(\text{SCN})_2^-$, it can adsorb at 560 nm. This mechanism explains the decrease in absorption at lower wavelengths and the increase at higher ones. This decrease in absorption at 505 nm could even be enhanced by the fact that silver interstitials are extracted by SCN^- from the monomers (505 nm) and are partly re-deposited at surface cells with more sulphur atoms, which are deeper interstitial silver ion traps (ISI-traps)². This silver transporting mechanism can be due to pure silver thiocyanate complexes, but bromide ions can play the same role since the concentration of bromide and thiocyanate are of the same order (1 mmole / mole Ag); AgBr_2^- and $\text{Ag}(\text{BrSCN})^-$ could also be a transporter for silver ions. This mechanism may explain alternatively the enhanced rate of sulphur and sulphur-plus-gold sensitization, which was found earlier⁴ and ascribed to enhanced agglomeration of Ag_2S . The effects on the long wavelength sensitivity and temperature dependence suggest that thiocyanate modifies the trap depth distribution, namely producing relatively more deep traps⁹. This decrease in the energetic LUMO level of the cluster could be demonstrated by a decrease in development time for fog centers when thiocyanate is added. The creation of deeper traps could also be explained by the supply of silver ions by the thiocyanate 'transporter' ion to the silver sulphide clusters.

2. Influence of thiocyanate on the sulphur + gold ripening

There is not only a complexation of thiocyanate ions with free and interstitial silver ions as mentioned above, but also with gold ions if they are present in the solution. After an emulsion was sensitized with sulphur, radioactive gold (198) ions were added to this emulsion, which became incorporated into the formed silver sulphide clusters. After 60 minutes thiocyanate ions were added to remove gold ions out of the cluster. The uptake of gold ions was monitored as a function of the reaction time for different sulphur concentrations added (diacetyl thiourea) as can be seen in figure 4. The concentration of gold added was equal to the concentration of sulphur added, expressed as respectively Au and S. The curves start at a reaction time of 1 hour, which is the end of the sulphur ripening time and the moment that gold ions are added. Note that the gold uptake is already stable after 30 minutes of reaction. After 1.5 hours of gold reaction 10 mmole KSCN / mole Ag is added to the emulsion.

For high concentrations of sulphur added there is a large decrease in gold uptake (6 S - 4 S), what cannot be found for the lower sulphur concentration (1 S - 2 S) due to the relatively larger errors. The removal of gold by thiocyanate out of the silver sulphide clusters occurs at very low SCN^- concentrations (< 1 mmole KSCN / mole Ag) and reaches a saturation level as a function of the thiocyanate concentration added, indicating that only a certain fraction of the gold ions is removable. First it was thought that gold ions bound between two sulphur atoms are removed, while the ones bound with three will stay in the cluster. This would implicate that at higher sulphur concentration (where

larger clusters are formed) less gold can be removed than at low sulphur concentration. Since this is not the case (see Figure 4), a more consistent mechanism had to be found. This thiocyanate level where a decrease in gold concentration is detected, is also dependent on the concentration of sulphur and gold added to the emulsion. At extremely high levels of sulphur (20 S + 20 Au) the gold uptake level was saturated at 2 mmole KSCN / mole Ag added instead of 0.5 mmole KSCN / mole Ag.

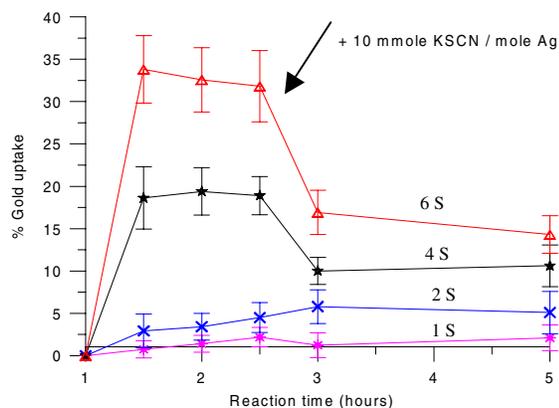


Figure 4. Influence of the addition of 10 mmole KSCN / mole Ag on the gold uptake (addition of Au after 60' sulphur, 60 °C, $u_{Ag} = 84$ mV, $pH = 5.60$; $Au / S = 1$)

In figure 5 the evolution of the diffuse reflectance spectra on gold removal is plotted for the three wavelengths of deconvolution. On the top of the curve the additions are mentioned at their corresponding reaction time. During the first 1.5 hours the Kubelka-Munk values for the pure sulphur sensitization are measured. Addition of gold (after 1.5 hours) results in a large decrease in the KM values, due to the suppression of the silver interstitials of the cluster². The KM value remains constant for the following hour, until 10 mmole / mole Ag of thiocyanate is added. Addition of this quantity of SCN^- gives back an increase of the KM value, however not the same at all wavelengths. The KM value at 505 nm, which is the top curve in Figure 5, is restored completely, while at 560 nm this is only true for circa 50 %, and at 610 nm it is even hard to distinguish any increase compared to the sulphur plus gold case. All data points in figure 5 are obtained via deconvolution of the diffuse reflectance spectra.

These effects of thiocyanate on the sulphur-plus-gold sensitized crystals can be explained for both tracer analysis and diffuse reflectance spectroscopy. Besides deposition of gold ions bridging two or three sulphur atoms, gold ions may also replace silver ions, which are part of a subsurface cell of sulphur (type 2 gold ions in Figure 6). These substitutional gold ions are positioned in the AgBr lattice, bound between a sulphur and bromide ion, and can again easily be exchanged for Ag^+ . Due to the stronger complexation of gold with thiocyanate and sulphite than

with silver ions, these 'gold lattice ions' can be easily removed out of the cluster when these compounds are added to the emulsion. However, the gold ions, which are bound with two or three sulphur atoms, are not removed. This means that during our tracer procedure, when treating with thiocyanate and washing with sulphite, the number of gold ions found incorporated is indeed proportional to the concentration of higher cluster forms⁵.

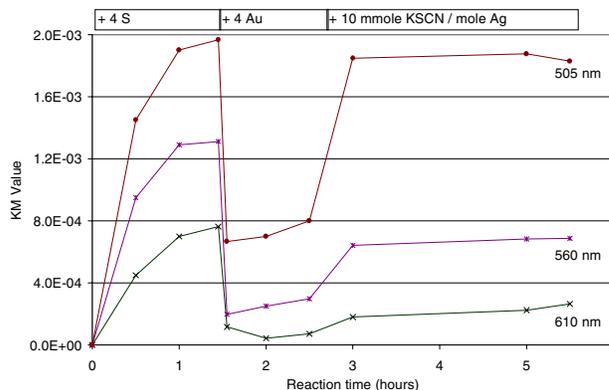


Figure 5. KM value at three wavelengths of deconvolution for an emulsion sensitized with sulphur (4 S for 1.5 hours) followed with gold (4 Au for 30 min) and followed with thiocyanate (10 mmole KSCN / mole Ag); (65 °C, $u_{Ag} = 84$ mV, $pH = 5.60$)

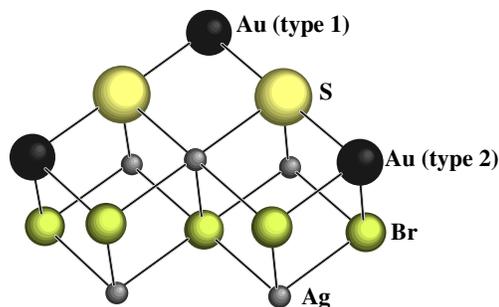


Figure 6. Dimer of sulphur with 3 gold ions incorporated; 1 gold ion bridging 2 sulphur atoms (type 1) and 2 substitutional gold ions (type 2)

The rate at which the KM value increases after addition of thiocyanate depends strongly upon the concentration of thiocyanate added. At high concentrations a saturation level is immediately reached (Figure 5), while at low concentrations the KM value increases gradually. The fact that the KM value at 505 nm is completely restored means that for this sulphur species there are no gold ions which are bridged between sulphur atoms, only gold ions incorporated in the subsurface cell. This indicates that an isolated sulphur atom (monomer) causes the absorption at 505 nm (i.e. absorption of the monomer).

Depending on the stability constants for aurous complex ions it is thus possible to remove different types of

gold ions as shown in the table below. From these different interactions it is possible to obtain detailed information about the silver sulphide cluster distribution⁵.

Table 1. Removal of different gold compounds depending on the ligand

Added ligand	Type of removed gold ions
H ₂ O	Free gold ions in solution
SO ₃ ²⁻	Free and adsorbed gold ions
SCN ⁻ + SO ₃ ²⁻	Free, adsorbed and substitutional gold ions in silver sulphide clusters
CN ⁻	All different types of gold ions

Conclusions

For sulphur sensitized emulsions two different cases of thiocyanate addition were studied:

1. When thiocyanate is added prior to sulphur, it rearranges the surface by increasing the number of kink sites, so the sulphur deposition rate is enhanced but the supply of silver interstitials is limited.
2. Addition of thiocyanate after the sulphur reaction results in the formation of SCN⁻ complexes with silver, from which a silver is more easily deposited in a surface cell of the deposited silver sulphide clusters (silver transporter).

The increased rate of sensitization found earlier⁴ suggests that thiocyanate orients interstitials preferably to dimers and higher polymers, which are potential sensitization centers. Also HIRF decrease by thiocyanate may be explained on the same basis.

For sulphur-plus-gold sensitized emulsions it was observed that a fraction of the gold ions could be removed out of the silver-gold-sulphide clusters by addition of thiocyanate ions and subsequent washing with a sulphite solution. Two different types of gold ions are present in the silver sulphide clusters:

1. gold ions which are substitutional for silver (bound between sulphur and bromide ions): these can be removed by thiocyanate
2. gold ions which bridge two or three sulphur atoms: these can neither be removed by thiocyanate nor by washing with a sulphite solution

It is only after treating the emulsion with thiocyanate and washing the coated emulsion with a sulphite solution that the concentration of gold ions is related to the cluster size distribution (ratio monomers / dimers). Incorporation of gold ions suppresses the optical absorption in DRS. Since the optical absorption at 505 nm can completely be restored by addition of thiocyanate it is assumed that the entity

absorbing at this wavelength is a monomer of silver sulphide. From these results it is again clear that the combination of DRS and tracer analysis is a powerful tool in studying chemical sensitization of photographic emulsions.

References

- 1 E. Charlier, M. Van Doorselaer, R. Gijbels, R. De Keyzer, I. Geuens, *J. Imag. Sci. Technol.*, 44, 243 (2000).
- 2 M. Van Doorselaer, E. Charlier, A new approach to the mechanism of sulphur and sulphur + gold, *Proc. ICPS Conference 98*, pg. 267, (1998).
- 3 E. Charlier, R. Gijbels, M. Van Doorselaer, R. De Keyzer, D. Vandebroucke, I. Geuens, Role of silver interstitials in silver sulphide clusters formed during chemical sensitisation, *Proc. ICPS Conference '98*, pg. 455. (1998).
- 4 M. Van Doorselaer, *Proceedings of SPSE east-west meeting, Hawaii* (1988).
- 5 E. Charlier, M. Van Doorselaer, R. De Keyzer, R. Gijbels, Determination of the silver sulphide cluster size distribution via computer simulations, *Proc. AgX 2000* (2000).
- 6 H. Frieser, G. Haase, E. Klein, *Die Grundlagen der Photographischen Prozesse mit Silverhalogeniden, Band 1*, Akademische Verlagsgesellschaft, pg. 526, (1968).
- 7 S. Ehrlich, *Photogr. Sci. Eng.*, 23, 348 (1979).
- 8 S. Ehrlich, *J. Imag. Sci. Technol.*, 37, 73 (1993).
- 9 R. Hailstone, Internal publication Agfa-Gevaert N.V., (1998).

Acknowledgement

This work is partly supported by the Federal Services for Scientific, Technical and Cultural Affairs (DWTC/SSTC) of the Prime Minister's Office (contract nr. IUAP IV, P4/10).

Biography

Evan Charlier received his Ph.D. in Chemistry at the University of Antwerp (Belgium) in early 2000, in close collaboration with Agfa-Gevaert N.V. The title of his thesis summarises nicely the main focus points of his research "Elucidating the structure and functioning of sulphide clusters grown epitaxially on the surface of AgBr microcrystals by using a combination of diffuse reflectance spectroscopy and tracer analysis".