

Interactions of Co-adsorbed Spectral Sensitizers on the Surface of Silver Halide Microcrystals

J. Van Nylen, and E. Goovaerts

Physics Department, University of Antwerp - CDE, 2610 Wilrijk, Belgium

P. Callant, K. Viaene, and R. De Keyzer

R&D Laboratories, Agfa Gevaert N.V., 2640 Mortsel, Belgium

Abstract

In many silver halide (AgX) technology based imaging materials, two spectral sensitizers are co-adsorbed on the AgX microcrystal surface in order to adjust the optical spectrum. More importantly, this can give rise to supersensitization, which is crucial for the sensitivity of such systems. Detailed knowledge of these phenomena allows the optimization of the spectral sensitivity and overall image formation efficiency.

Our spectroscopic study of the underlying interactions uses a combination of Electron Spin Resonance (ESR) and Diffuse Reflectance Spectroscopy (DRS) to identify the dye radicals formed after electron transfer, providing crucial information about the supersensitization mechanism involved.

Identification of dye radicals with ESR is based on determination of their g -values and supported by the DRS observation of new electronic transitions.

Additional information is obtained from studying the kinetics of the light-induced radical formation and decay.

Unfortunately, an unambiguous identification of the radicals is not always possible. Practical limitations of the experimental procedure, as well as perspectives for improvements are discussed.

Introduction

The use of a combination of spectral sensitizers, co-adsorbed on the same silver halide substrate, and in which one of them is used as a supersensitizer, has been known for a long time.¹ Various mechanisms have been used to describe the nature of the interaction between both dyes, giving rise to the observed supersensitization effect.² The two main mechanisms are aggregate partitioning^{3,4} and hole trapping.⁵⁻⁷ In order to optimize the supersensitization effect, detailed knowledge of the mechanisms involved, and of the processes acting on the dye radicals is essential. Identification of the dye radicals formed upon excitation of the main dye, provides information about which supersensitizing mechanism is involved. When supersensitizer radicals are detected, hole trapping has occurred, while aggregate partitioning is most likely when only main sensitizer radicals are detected.^{8,9}

The identification of the radicals formed can be done with ESR,^{10,11} as well as DRS.¹² With ESR the identification is based on features of the light-induced spectrum like: line shape and g -value. Distinction between

sensitizer radicals based on the g -value is a challenging task since the organic dye radicals are all located around $g = 2.005$,¹⁰ and a determination of the g -value with high precision is necessary. The optical detection of sensitizer radicals is based on the appearance of two new absorption bands in the DRS spectrum upon excitation.¹²

Information about the processes acting on the dye radicals can be obtained from the line width of the ESR spectrum and the kinetics of the dye radicals. Aggregation of the sensitizers usually gives rise to highly mobile radicals, which narrows the ESR line width. Aggregate partitioning can be observed by an increase in line width upon addition of the supersensitizer to the system. The decay of the radical concentration in the dark can give information about the hole trapping mechanism: a slower decay rate indicates a more stable hole on a higher lying SOMO level.

Experimental

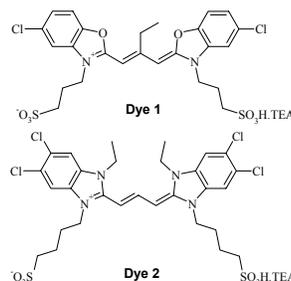


Figure 1. Molecular structure of the two green spectral sensitizers investigated in this work.

In this work systems were studied that consist of green sensitized cubic AgBr microcrystals with an edge length of 0.556 μm . Two different dyes were used, either adsorbed alone or in combination. The molecular structures of the two dyes are shown in figure 1. Dye 1 was added in a concentration such that the entire surface was covered. Dye 2 was added in a concentration corresponding to 10 % of crystal surface coverage.

The spectral excitations were done with the 514.5 nm line from an argon laser (50 mW, i.e. about 10 photons per molecule per second).

The ESR experiments were performed on a Bruker ESP300E CW X-band (9.5 GHz) setup. Transient ESR intensities are measured at the field position of the maximum of the first derivative spectrum, which is

proportional to the peak-to-peak intensity. The DRS spectra were measured using a Shimadzu 3101PC UV-vis-NIR spectrophotometer, with an integrating sphere.

Results and Discussion

In a previously studied dye combination of a red sensitizer and a UV sensitive supersensitizer,⁸ aggregate partitioning was demonstrated using the combination of ESR and DRS. The red sensitizer radicals were observed with ESR, but since no supersensitizer radicals could be detected, the dye radicals in the combined system could not be unambiguously assigned to red sensitizer radicals. The optical detection of the radicals with DRS provided the necessary information, that indeed also red sensitizer radicals were formed in the combined system. The effect on the ESR line width corresponding with the aggregate partitioning mechanism was also observed.

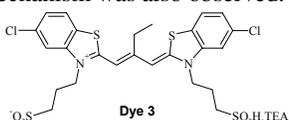


Figure 2. Molecular structure of the red sensitizer Dye 3

This is in contrast to a combination of the J-aggregating green sensitizer Dye 1 with a very similar, but red sensitive Dye 3, for which ESR provided identification of the radicals. The radical lifetime in this combination was too short, and proved to be the limiting factor for the identification of the radicals with DRS. The ESR line shape of both types of radicals furthermore proved to be very similar: a narrow line resulting from the radical mobility in the J-aggregate. The identification of the formed dye radicals based on the g -value indicated that hole trapping on the red sensitizer occurred after excitation of the green dye.

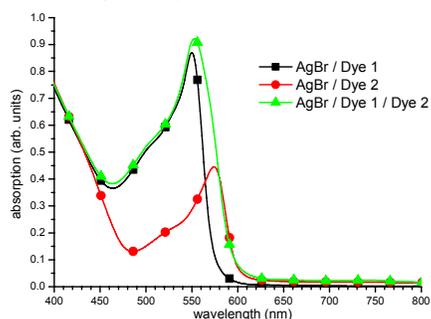


Figure 3. Absorption spectra of the studied samples.

In the present combination two green sensitizers are used that both give rise to a J-aggregate on the AgBr, as can be seen in figure 3. In these systems no distinction between the radicals was possible with ESR, because in addition to the similar line shape, their g -values is equal within experimental accuracy, as can be seen in figure 4. Based on sensitometric results, hole trapping on Dye 2 was suggested as the supersensitization mechanism in this dye combination.¹³ The kinetics of the dye radicals was used to find more evidence supporting the hole trapping mechanism.

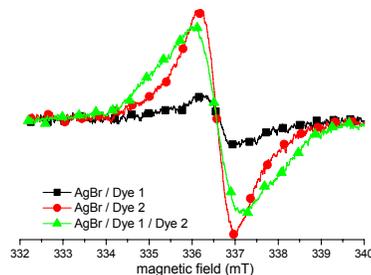


Figure 4. ESR spectra upon spectral excitation of the investigated system.

Individual Sensitizers

The radical concentration as observed with ESR is determined by the equilibrium between the growth and decay processes. These processes can be revealed by kinetics experiments, in which the radical concentration is monitored as a function of excitation and decay time. The radical concentration is proportional to the integrated intensity of the ESR spectrum.¹⁴ However recording a complete ESR spectrum is not possible in situations where the decay of the radicals is faster than the time it takes to record a full spectrum with a reasonable signal/noise ratio. When the line width of the spectrum doesn't change in time, the peak-to-peak amplitude of the spectrum can be used to study the different processes determining the radical concentration.

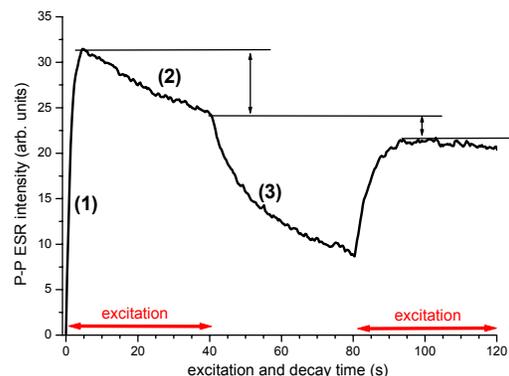


Figure 5. Contribution of three different processes on the growth and decay of radical concentration in the AgBr / Dye 2 sample. The arrows mark the excitation periods.

In figure 5 the typical evolution of the radical concentration in the AgBr / Dye 2 system is shown. First of all there is the photo-induced creation of the dye radicals, that can be observed from the rise of the ESR intensity [(1) in figure 5]. For stable radicals, the ESR intensity will saturate at a certain level corresponding to the situation in which all dye molecules have been converted into dye radicals. If on the other hand the radicals decay the saturation concentration is determined by the growth and decay rates of the dye radicals. Secondly there is a decay of the radical concentration during the excitation [(2) in figure 5]. It can be deduced from this figure that this decay during excitation reduces the radical concentration irreversibly, since the second excitation of the same system results in a lower radical concentration as the first one. When the excitation is

stopped there is a strong decrease in the radical concentration [(3) in figure 5]. During this dark period, the dye molecules are reset, making them available again for a consecutive excitation. For the reversible process, dye induced latent image regression was suggested to be the responsible process in the time range that is observable with conventional ESR. For the irreversible process a radical dimerization process is suggested.¹⁵

As can be seen in this figure 6, in which the kinetics results of the same sample are shown, but for four consecutive excitation (marked by the arrows) and decay periods, the rates of these three processes are not time independent. During the second excitation, the slope of the increasing radical concentration is not as steep as during the first excitation and the irreversible process is much less pronounced, revealing more clearly the actual growth of the radical concentration. An observation that is even clearer when comparing the last excitation with the first one. The changes in growth curve are due to a different radical formation efficiency, most likely caused by the fact that the starting conditions for the first excitation are differing from those of the second and later excitations. In the latter cases, there are already dye radicals present inside the aggregate. This means that the system can't be described as a set of individual dye molecules that get excited and oxidized independently from each other. These changes rather reflect the behavior of the entire aggregate instead of the individual molecules.

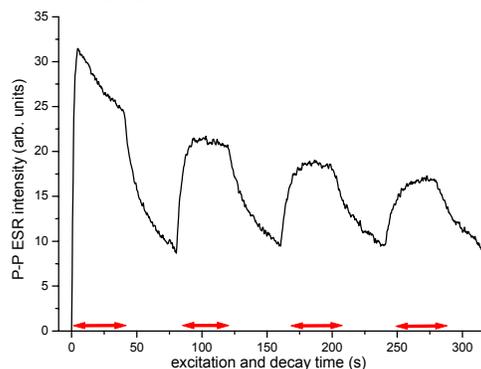


Figure 6. Growth and decay of radical concentration during four consecutive excitation and decay periods on the Dye 2 sample. The excitations are marked by the arrows.

It was shown both by Lenhard et al.¹⁶ and Kawasaki et al.,¹⁷ that the oxidized dye molecules (radicals) present inside the J-aggregate, influence the oxidation potential of the aggregate. They both studied (electro)chemically generated dye radicals in J-aggregates. Lenhard studied long-lived dye radicals on AgBr generated by one electron oxidation by a ferro cyanide redox solution. Kawasaki investigated very short lived dye radicals generated by fast-scan cyclic voltammetry in a J-aggregate adsorbed on a self-assembled cystamine monolayer on a Au(111) model surface. They both proposed an increase of the oxidation potential E of the J-aggregate that can be described using a Nernst equation:

$$E = E_0 + RT/F \ln ([\text{Dye}^{\bullet}]/[\text{Dye}])$$

in which R is the gas constant, T the temperature and F the Faraday constant. E_0 is the standard potential. From this equation it is clear that, under the ideal Nernst conditions

(a dye radical completely surrounded by the normal dye molecules), an increase in the radical concentration $[\text{Dye}^{\bullet}]$ relative to the original dye molecule concentration $[\text{Dye}]$ reduces the oxidation potential E . Since the energy gap ($E = h\nu$) is almost constant, this results in a reduced electron transfer rate from the aggregate for the second excitation and the slope in our kinetics curve will decrease.

Based on Kawasaki's observation a non-ideal Nernst behavior caused by the interaction between dye positive holes at higher radical concentrations, it seems plausible that also in the present work a deviation of the ideal behavior arises, since the high excitation intensities used together with the very suitable position of the dyes' LUMO level relative the conduction band of the AgBr give rise to a rapid build up of interacting radicals. This deviation from the ideal behavior will only increase the oxidation potential more rapidly,^{16,17} supporting the statement that also in this system the observed decrease in growth rate for the secondary excitations are caused by a drop in the Dye 2 J-aggregate's HOMO level, induced by the presence of dye radicals.

Further evidence for the fact that the growth rate is decreased due to the presence of dye radicals in the aggregate at the start of a new excitation can be obtained from studying a system sensitized by Dye 1, in which the dye radicals have a shorter life time compared to those of Dye 2. Here the radicals decay completely in the same time span (figure 7) in the dark, such that the starting conditions for each excitation are very similar, corresponding to the non-oxidized J-aggregate. It is clear that the growth rate of the radical concentration is now basically the same for each consecutive excitation, consistent with the effect of the radical concentration on the oxidation potential of the aggregate.

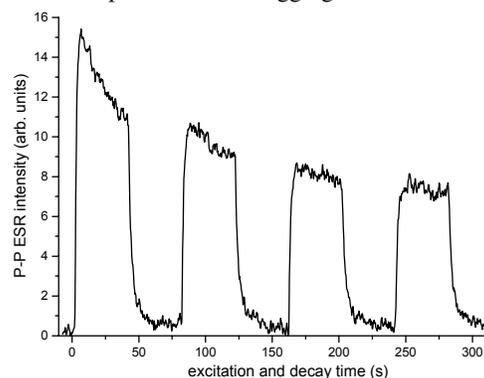


Figure 7. Growth and decay of the radical concentration during consecutive excitation and decay periods in the Dye 1 system with a high reversible decay rate of the radicals.

In the AgBr / Dye 1 system (figure 7), only the irreversible decay rate is reduced in the consecutive excitations. This corresponds with a model which involves radical dimerization, since the formed radical dimers partition the aggregate, and therefore the radical mobility, and hence the chance for a radical to find another one, is reduced.

In figure 6 also a reduction of the reversible decay rate can be observed after the consecutive excitations. Since the reversible decay is due to latent image

destruction, and these centers have their energy level gradually lowered relative to the SOMO of the dye radical by the excitations, it is expected that it gradually becomes more difficult to oxidize these clusters. As a result the latent image regression is reduced, slowing down the reversible decay process.

For the system sensitized by Dye 1 (figure 7), the decay rate is not slowing down after the consecutive excitations. This is most likely due to fact that the latent image clusters are not large since the amount of generated radicals is lower in this system compared to that of figure 6, as can also be verified in figure 4. This is caused by a lower electron transfer efficiency, due to the fact that the LUMO of Dye 1 is considerably lower than that of Dye 2.¹⁸

Co-adsorbed Sensitizers

In the system where Dye 1 and Dye 2 are co-adsorbed on AgBr (figure 8), the interpretation of the growth and decay of the radical concentration is more difficult. From the ESR spectrum shown in figure 4, it can be deduced that this spectrum no longer consists of a single line, but has two or more contributions, corresponding to different dye phases on the AgBr surface. The dark decay for this system has two distinct components: a very fast one (Dye 1) and a slower one (Dye 2). The latter one is even slower compared to the AgBr / Dye 2 *J-aggregate* system. This is likely due to a higher SOMO level of the Dye 2 monomer radical, supporting the proposed hole trapping mechanism in this dye combination.¹³ The radical concentration growth doesn't slow down as much either. This is explained by a reduced mobility of the Dye 2 radicals, most likely located at the domain edges, limiting their influence on the aggregate's oxidation potential.¹⁷

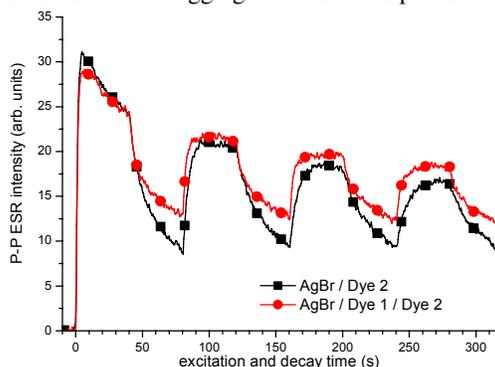


Figure 8. Comparison of the growth and decay of the radical concentration for the system in which only Dye 2 is adsorbed, and for the system where both dyes are adsorbed onto the AgBr.

Conclusion

Assignment of the radical structure in sensitized AgBr systems, based on properties of the ESR or DRS spectra, can yield information about the interaction between co-adsorbed dyes. When those approaches fail, information can be gathered from kinetics studies. This is only successful when the individual dye systems are well

understood, before looking at the combined system, in which contributions involving both dyes are to be expected.

Acknowledgements

This work was supported by the 'Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT)'.

References

- O. Bloch and F. F. Renwick, *Photogr. J.* **60**, 145 (1923).
- P. B. Gilman, *Photogr. Sci. Eng.* **18**, 418 (1974).
- W. West and B. H. Carroll, *J. Chem. Phys.* **15**, 529 (1947).
- A. E. Rosenoff, K. S. Norland, A. E. Ames, V. K. Walworth, and G. R. Bird, *Photogr. Sci. Eng.* **12**, 185 (1968).
- P. B. Gilman, *Photogr. Sci. Eng.* **12**, 230 (1968).
- P. B. Gilman and T. D. Koszelak, *J. Photogr. Sci.* **21**, 53 (1973).
- J. E. Jones and P. B. Gilman, *Photogr. Sci. Eng.* **17**, 367 (1973).
- J. Van Nylen, D. Schoemaker, E. Goovaerts, P. Callant, K. Viaene, and R. De Keyzer, accepted for publication in *J. Appl. Phys.* **96** (2004).
- J. Van Nylen, E. Goovaerts, D. Schoemaker, P. Callant, K. Viaene, and R. De Keyzer, *ICIS'02 Proceedings*, 95 (2002).
- T. Tani and Y. Sano, *J. Photogr. Sci.* **27**, 231 (1979).
- T. Tani, *J. Appl. Phys.* **62**, 2456 (1987).
- J. R. Lenhard and A. A. Muentner, *J. Electrochem. Soc.* **134**, 97 (1987).
- R. De Keyzer and P. Callant, in *IS&T's 1998 PICS Conference Proceedings*, Portland, 1998, pg. 311.
- T. Ceulemans, D. Schoemaker, D. Vandenbroucke, and R. De Keyzer, *J. Appl. Phys.* **82**, 1776 (1997).
- J. R. Lenhard and R. L. Parton, *J. Am. Chem. Soc.* **109**, 5808 (1987).
- J. R. Lenhard and B. R. Hein, *J. Phys. Chemistry* **100**, 17287 (1996).
- M. Kawasaki, D. Yoshidome, T. Sato, and M. Iwasaki, *J. Electroanal. Chem.* **543**, 1 (2003).
- J. P. Zheng, A. G. DiFrancesco, R. K. Hailstone, P. Callant, and R. De Keyzer, *Imaging Sci. J.* **50**, 63 (2002).

Biography

The primary author (JVN) graduated from the University of Antwerp in 1999 with great honours. In his graduation thesis, *ESR Study of Silver Behenates*, he investigated the optically induced paramagnetic radicals in thermo- and photothermographic materials. He is about to defend his PhD entitled: *Supramolecular Functional Systems: Interaction of Molecular Components with Microcrystalline Semiconductors* in which he studied the interaction of co-adsorbed sensitizers on AgHal surfaces both optically (DRS) and with ESR.