Investigations on Photographic Sensitivity in Connection with Modification of AgBr Crystal Surfaces by Adsorption of Surface Active Substances

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Introduction

The problem of the interstitial silver ion concentration [Ag$^+$_] was mentioned frequently in earlier papers. In spectral sensitization of silver halides the coadsorption of different adsorbents was introduced as very effective [Ag$^+$_] adjusting method. The Ag$^+$_ concentration increased by adsorption of cyanine dye can be counteracted by sulfur containing crown compounds and podands as well as antifoggants and stabilizers.$^{1,2}$

This paper will illustrate the necessity of consideration of not only Ag$^+$ but also all charge carriers (electrons, holes and Ag$^+$) involved in latent image formation. To investigate this problem octahedral AgBr and AgBrI emulsions were observed regarding to their spectral sensitivity, ionic (dielectric loss, DL) and electronic properties (photo-emf). Dye concentration, coronand concentration and concentration of homogeneous distributed iodide were used as variation parameters influencing the latent image formation.

Dielectric loss measurements were used for characterization of interstitial silver ion concentration. Photo electromotive force (photo-emf) measurements were performed in order to get information about the formation and reaction of photochemical generated charge carriers. The coherent view of both the ionic and electronic situation in a AgBrI micro crystal provides a more complete picture about photoinduced reactions involved in the latent image formation.

Experimental

Emulsions
The silver halide emulsion grains were prepared by means of conventional pAg controlled double jet precipitation. The AgBr microcrystals used in the experiments were monodisperse and octahedral (edge length = 0.5 μm).

Our results were performed with compound 1 shown in fig. 1 as an example for sulfur containing crown compounds and podands.

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Figure 1: Structure of the used podand as an example for sulfur containing crown compounds and podands

Dry sheets of the emulsions (0.12 mm thickness) were prepared by standard procedures. A symmetrical benothiazole trimethine was used as sensitization dye.

Dielectric Loss Measurements
Conductivity measurements were performed at room temperature in a frequency range between 1 kHz and 13 MHz using a HP Impedance Analyzer 4192A. A dried emulsion sample was mounted between two plates of the capacitor and the impedance of the sample was measured as a function of frequency. The frequency at the maximum dielectric loss $f_{\text{max}}$ is proportional to the product of interstitial’s concentration and mobility. $^3$

$f_{\text{max}}$ is used for further discussion.

Measurements of Photo-emf
The photo-emf measurements were described by MUELLER et al.$^4$ A N$_2$-Laser ($\lambda = 337$ nm; $t_{\text{ff}} = 0.5$ ns; 100 μJ per pulse) and a 200 MHz storage oscilloscope were used in all experiments. The sign of the photo-voltage $U$ was measured at the illuminated front electrode. Fig. 2 shows a photo-emf signal.
A signal as shown in fig. 2 delivers the information about sign (characterizes the type of semiconductor); \( U_{\text{max}} \) (proportional to the maximum number of photogenerated charge carriers) and half lifetime \( t_{1/2} \) of signal (proportional to lifetime of electrons).

It was necessary to analyze the signals as two partial processes which differ in their rate constants for decay behavior. The signals were analyzed by a biexponential model (compare eq. 1) to grasp both rate constants.

\[
U(t) = U_1^0 \cdot e^{-k_1 t} + U_2^0 \cdot e^{-k_2 t} \quad \text{eq. 1}
\]

The parameters \( U_1^0, U_2^0, k_1 \) and \( k_2 \) of biexponential model were used for further discussion.

**Results and Discussion**

**Crown compounds**

Fig. 3 shows the influence of compound \( 1 \) on the DL of a silver bromide octahedral emulsion. The frequency at the maximum of DL is shifted to lower frequencies. Ag\(^{+}\) concentration is decreased.

This observation can be explained in terms of complexation of Ag\(^{+}\) by podands comparable as in solutions.

Figure 4 shows the behavior of calculated rate constants \( k_1 \) and \( k_2 \) from the photo-emf signal with increasing concentration of podand \( 1 \) in the emulsion.

**Sensitization dye**

The change of \( f_{\text{max}} \) for an octahedral silver bromide emulsion with rising dye concentration is shown in figure 5. The sensitizer adsorbed at the AgBr grain surface influences mainly the shift of the high frequency (hf) peak. The hf- peak characterizes the Ag\(^{+}\)-concentration of the subsurface region. A distinct peak separation is observed above an dye concentration of 200 \( \mu \text{mol} / \text{mol Ag} \). There the hf peak is shifted to frequencies > 13 MHz. The low frequency (lf) peak is almost uninfluenced.
Iodide (homogeneous distribution)

Figure 7 shows the influence of homogeneous distributed iodide in AgBr octahedral crystals on the DL. Iodide increases the interstitial concentration in the whole crystal, however stronger in subsurface region than in the bulk.

The behavior of rate constants $k_1$, $k_2$ of the different processes is shown in figure 8 in dependence on iodide concentration. Both processes accelerate in a different way by increasing incorporation of iodide in the crystal. A comparison of the DL values obtained by increasing dye concentration and increased iodide concentration shows that both (iodide and dye) will increase the Ag$^+$-concentration. But iodide accelerates the photo-emf decay processes compared with the dye see fig. 6.

A further comparison between the influence of podand and dye reveals that they influence the DL in an opposite way. In contrast to this both (podand and dye) will effect photo-emf by decelerating the slower part of decay curves. This result indicates, that the decay behavior depends not only on Ag$^+$-concentration.

Processes caused by the light absorbed in the dye layer have to take into account by the interpretation of the rate constants.

Figure 5: Frequency at maximum of dielectric loss $f_{\text{max}}$ for AgBr octahedra versus concentration of dye; dashed line: high frequency peak; solid line: low frequency peak

Figure 6: Rate constants $k_1$ (●) and $k_2$ (●) from the biexponential model (eq. 1) versus concentration of dye

Figure 7: Frequency at maximum of dielectric loss $f_{\text{max}}$ for AgBr octahedra versus concentration of iodide; dashed line: high frequency peak; solid line: low frequency peak

Figure 8: Rate constants $k_1$ (●) and $k_2$ (●) from the biexponential model (eq. 1) versus concentration of iodide
The photo-emf signal gets a positive sign by homogeneous distribution of iodide in the crystal. So the mobility of h+ should be reduced very strongly. The incorporated iodide will produce a „normal“ charge separation because of the moderate increase of Agi+ concentration, see fig. 7. This is in agreement with positive emf-sign.

A distribution of hole traps over the whole volume of the crystal follows from the homogeneous iodide distribution. That is in contrast to the traps situated at the surface caused by the dye. The gap between the valence and conduction band decreases by incorporation of 4 mole-% iodide in the crystal by 0.16 eV.

Both the homogeneous distribution of traps and the reduction of the band gap increase the probability of recombination of an electron (any location) and a hole (localized in a trap). The recombination is favored and signals have a faster decay.

Photographic Properties

Investigations of photographic sensitivity give a summarized information about the fate of all charge carriers involved in the photographic process. It was shown that the spectral sensitivity is increased and spectral desensitization is diminished by addition of a sulfur containing crown compound or podand. The Agi+ concentration influenced by the podand is visualized by measurements of DL. However, photo-emf measurements show in more detail the effect of the electron trap Agi+ as well as the effect of typical hole traps (iodide; dye) on both, electrons and holes. As a consequence in most cases DL-measurements do not correlate with sensitometric results. Correlations of photo-emf rate constants with sensitometric results should give a more insight into the reactions of photoinduced electron and hole pairs. Correlation of rate constants versus sensitometric results are show in figure 9 and 10. Figure 9 and 10 are examples for an emulsion containing 2 mol% iodide.

![Figure 9: Spectral sensitivity (*) and rate constant k1 (●) from the biexponential model (eq. 1) versus concentration of dye for an AgBr emulsion containing 2 mol% iodide](image)

![Figure 10: Spectral sensitivity (*) and rate constant k2 (●) from the biexponential model (eq. 1) versus concentration of dye for an AgBr emulsion containing 2 mol% iodide](image)

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References