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_i^+] was mentioned frequently in earlier papers. In spectral sensitization of silver halides the coadsorption of different adsorbents was introduced as very effective [Ag_i^+] adjusting method. The Ag_i^+ 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_i^+ but also all charge carriers (electrons, holes and Ag_i^+) 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 benzothiazole 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_{max} is proportional to the product of interstitial´s concentration and mobility.[3]

f_{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 (λ = 337 nm; $t_{1/2}$ = 0.5 ns; 100 μJ per pulse) and a 200 MHz storage oscilloscope were used in all experiments. The sign of the photovoltage U was measured at the illuminated front electrode. Fig. 2 shows a photo-emf signal.

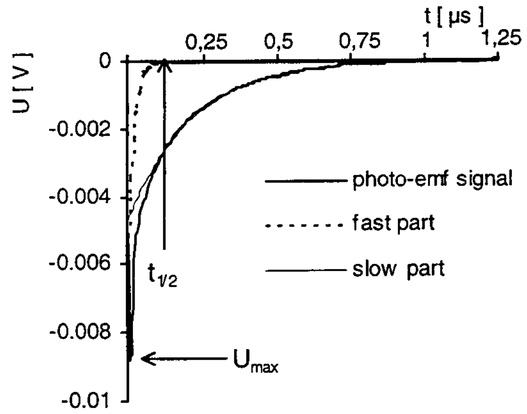

figure 2: photo-emf signal

A signal as shown in fig. 2 delivers the information about sign (characterizes the type of semiconductor); U_{max} (proportional to the maximum number of photogenerated charge carriers) and half lifetime $t_{1/2}$ of signal (proportional to life time 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 analyze by a biexponential model (compare eq. 1) to grasp both rate constants.

$$U(t) = U_1^0 \cdot e^{-k_1 t} + U_2^0 \cdot e^{-k_2 t} \qquad \textit{eq. 1}$$

The parameters U_0^1, U_0^2, 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_i^+ concentration is decreased.

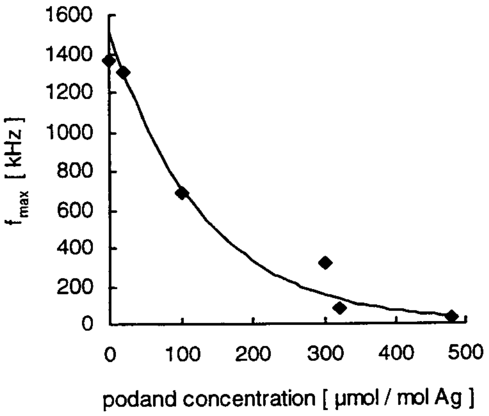

figure 3: Frequency at maximum of dielectric loss f_{max} for AgBr octahedra versus concentration of podand 1

This observation can be explained in terms of complexation of Ag_i^+ by podands comparable as in solutions.[5]

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.

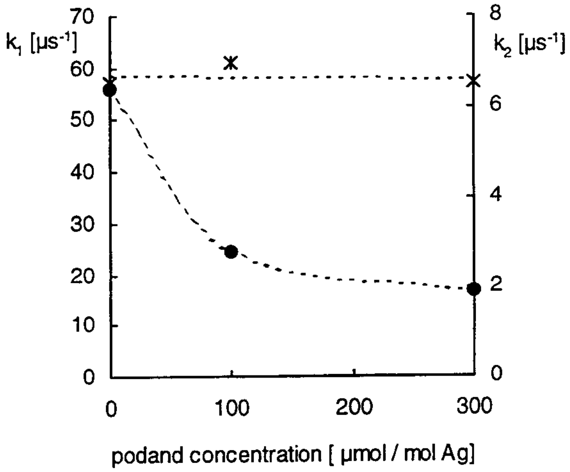

*figure 4: Rate constants k_1 (*) and k_2 (●) from the biexponetal model (eq. 1) versus concentration of podand* 1

The podand having a great influence on the Ag_i^+ concentration influences only the slower part of the photo-emf signal. k_1 is very fast. That indicates a diffusion control for the faster part of photo-emf decay. k_2 slows down with increasing podand concentration.

Sensitization dye

The change of f_{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_i^+-concentration of the subsurface region. A distinct peak separation is observed above an dye concentration of 200 µmol / mol Ag. There the hf peak is shifted to frequencies > 13 MHz. The low frequency (lf) peak is almost uninfluenced.[1]

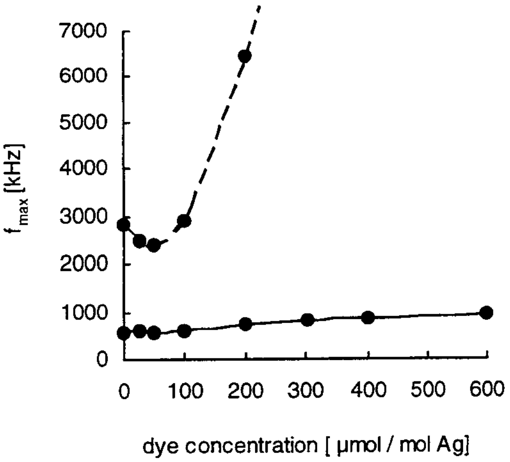

figure 5: Frequency at maximum of dielectric loss f_{max} for AgBr octahedra versus concentration of dye ; dashed line: high frequency peak; solid line: low frequency peak

Figure 6 shows the behavior of calculated rate constants k_1 and k_2 from the photo-emf signal. An increasing dye concentration causes a retarding of both processes, the slower and the faster.

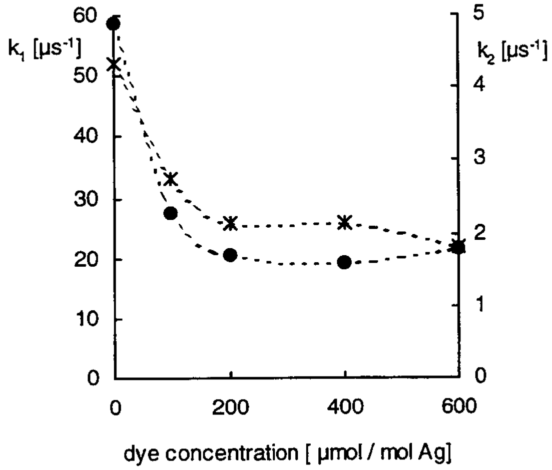

*figure 6: Rate constants k_1 (*) and k_2 (●) from the biexponetial model (eq. 1) versus concentration of dye*

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_i^+ -concentration.

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

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.

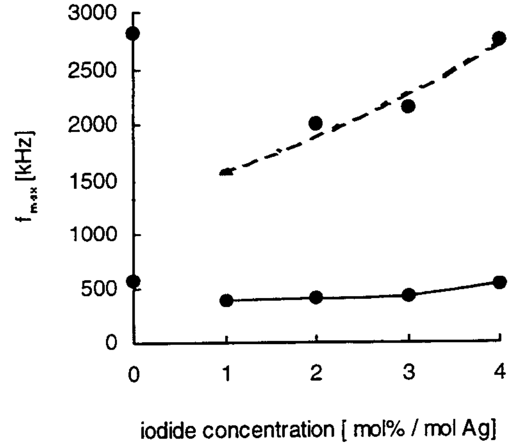

figure 7: Frequency at maximum of dielectric loss f_{max} for AgBr octahedra versus concentration of iodide; dashed line: high frequency peak; solid line: low frequency peak

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_i^+-concentration. But iodide accelerates the photo-emf decay processes compared with the dye see fig. 6.

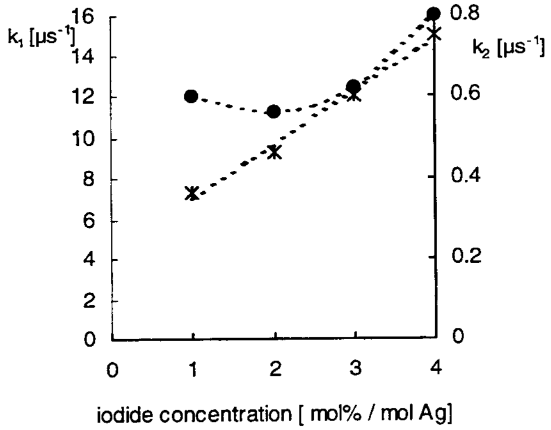

*figure 8: Rate constants k_1 (*) and k_2 (●) from the biexponetial model (eq. 1) versus concentration of iodide*

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 Ag_i^+ 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.[1] The Ag_i^+ 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 Ag_i^+ 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.

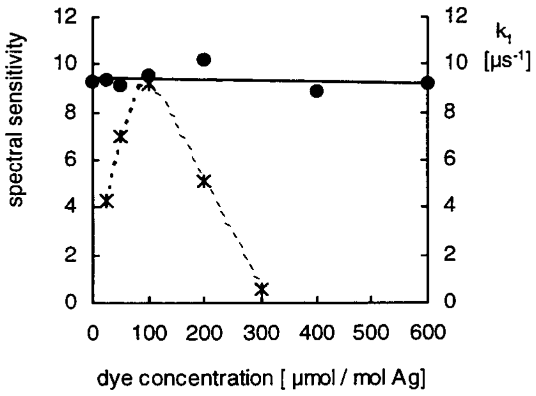

*figure 9: Spectral sensitivity (*) and rate constant k_1 (●) from the biexponetial model (eq. 1) versus concentration of dye for an AgBr emulsion containing 2 mol% Iodide*

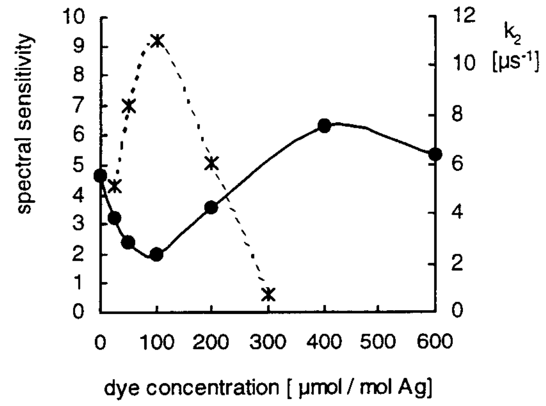

*figure 10: Spectral sensitivity (*) and rate constant k_2 (●) from the biexponetial model (eq. 1) versus concentration of dye for an AgBr emulsion containing 2 mol% Iodide*

The rate constants calculated from the photo-emf signals can be interpreted in terms of diffusion processes, chemical reactions, trapping/detrapping and recombination charge carriers. From this model k_1 corresponds to the reaction of electrons from flat traps (recombination or crossing in deeper traps). These processes proceed very fast. However k_2 corresponds to the reaction of electrons localized in deeper traps, for instance Ag_n (n>1). From this follows if k_2 is very low then available electrons are situated in deeper traps. A sufficient number of stable cluster may be formed. The sensitivity will be increased.

Same observations were made in the case of an emulsion without iodide and in the presence of sulfur containing coronands and podands.

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