Characterization of Photographic Emulsions by Dielectric Loss (DL) and Photo-EMF Measurements

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Abstract

The present paper reports photo-emf and dielectric loss measurements from photographic AgBr and $AgBr_xCl_{1-x}$ emulsions as a function of chemical sensitization using sulfur- and sulfur / gold-sensitization. Different kinetic treatment of photo-emf decay curves will be discussed.

Introduction

Chemical sensitization besides precipitation and spectral sensitization is one of the important steps in producing high sensitivity photographic emulsions. One of the most popular and successful chemical sensitization technique is sulfur sensitization (MANSFIELD, BENNETT, 1887; S.E. SHEPPARD, 1925). Ag_2S dimers may act on cubic and octahedral AgBr-emulsion crystals as electron traps, and clusters having an larger depth with > 400 meV may form fog centers (KANZAKI, 1990; TANI, 1997). High sensitivity connected with low level fog was realized using combined noble metal and sulfur sensitization (KOSLOWSKI, 1936). Effect of $[Au(Cl)_4]^-$ was described very early in substituting silver atoms by gold in ripening specks (F.W.H. MÜLLER, 1949).

Phenomenological description of the effect is done mostly by sensitometric measurements of the photographic sensitivity S, fog density D_{min} , maximum density D_{max} , and number N and distribution of development centers on the surface of individual emulsion crystals after illumination. More detailed investigation is possible by electrochemical methods or by direct electron microscopic detection of for instance Ag_2S-centers.

Investigating the influence of sensitization centers on primary reactions of photochemical produced charge carriers, electrons e^- and defect electrons h^+ , will reveal basic knowledge about latent image formation as key step within high sensitive silver halide emulsion crystals. A lot of work in this field of basic research was done by LEVY and TANI using photo charge or photo-emf measurements . A ´chemical´ model introduced by LEVY is used for interpretation of kinetic measurements, equation (1, 2):

$$e^- + h^+ \xrightarrow{k_2} \text{heat} \qquad (1)$$

$$e^- + Ag_i^+ \xrightarrow{k_1} Ag^0 \qquad (2)$$

K_2, k_1 hold for the second order rate constant of the recombination reaction of charge carriers , respective the pseudo-first order rate constant of the latent image forming silver clusters. In a chemical sensitization procedure k_1 reaches the top value at maximum sensitivity of the photographic emulsion. Around this value photo-emf traces show a crossing point at zero potential, e.g. the sign of the photo voltage changes its sign.

Equation (1,2) holds only for a homogeneous distribution of reacting species. This is true only for very small crystals or thin layers, but not for most emulsion crystals because light absorption according to LAMBERT-BEER law results in an inhomogeneous charge carrier distribution. A second problem of the kinetic model is the inability for describing decay traces with a crossing point at zero potential.

So we started a series of investigations with different photographic emulsions. The emulsions are characterized by DL- and photo-emf measurements. Raw data were treated using the kinetic model, see equation (1,2) and for comparison using a biexponential kinetic rate law, equation (3). This model is able to describe most decay traces including those ones with a crossing point:

$$U(t) = U_1^o \exp(-k_1 t) + U_2^o \exp(-k_2 t) \qquad (3)$$

The aim of the search is to study the influence of emulsion grain chemical composition, size and the kind of the ripening procedure on photo-emf kinetics. Farther, in some cases results of different kinetical treatment according to equations (1,2) or (3).

Experimental

AgBr or $AgBr_{1-x}Hal_x$ emulsions having different mole fraction $0 < x < 1$ of other halogenides and size of the crystals were prepared by potential controlled double jet precipitation. Chemical sensitization includes sulfur or combined gold/sulfur procedure. DL- and photo-emf equipment were described elsewhere.

Chemical sensitization was performed by standard procedures. Relative sensitivities S(rel) 0,1 or 0,2 over fog and fog densities D(min) were measured from cast emulsion sheets after illumination and development.

Results and Discussion

Sulfur Sensitization

Sensitivity S(rel) 0,1 over fog and fog density D(min) of an AgBr cubic emulsion were shown in fig. 1.

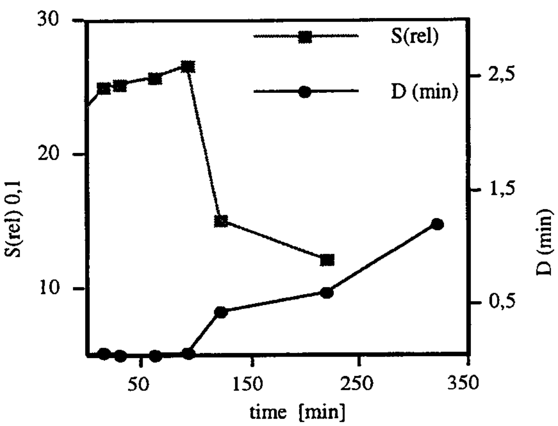

Figure 1: Sensitivity S(rel)0,1 and fog D(min) of a cubic AgBr emulsion after sulfur sensitization as a function of the time.

It is shown, that after 90 minutes desensitization becomes dominant parallel to the growing fog of the emulsion. The photo-emf results in fig. 2 reveal the standard picture: 1.) The Ag cluster formation constant k_1 show a maximum at maximum S(rel). 2.) The decay curves at 60 to 120 min. do show crossing points with the zero potential line. 3) Recombination rate constants k_2 have a minimum at maximum S(rel):

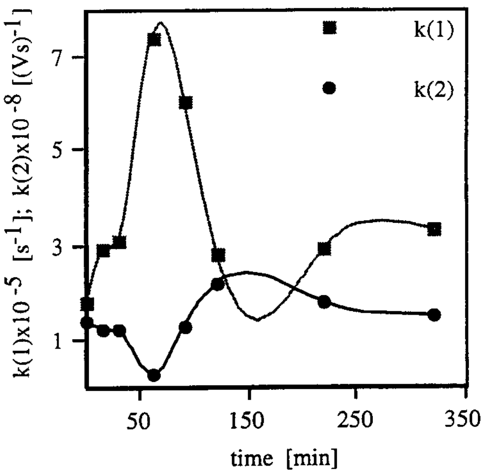

Figure 2: Rate constants $k_{1,2}$ from photo-emf measurements at different stages of S-sensitization according to fig. 1.

The incident maxima in S(rel) and k_1 can be interpreted in an optimum formation of latent image specks. This result indicates an optimum concentration of Ag_2S dimers formed within the sensitization procedure.

Sulfur / Gold Sensitization

S / Au sensitization was studied using an $AgBr_xCl_{1-x}$ cubic emulsion. Sensitometric results were shown in fig. 3 and fig. 4:

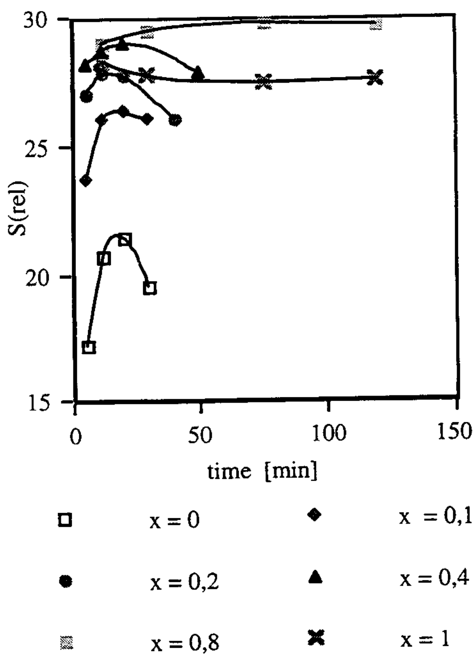

Figure 3: Sensitivity S(rel)0,2 of a photographic $AgBr_xCl_{1-x}$ emulsion (x = 0 ...1) as a function of S/Au sensitization.

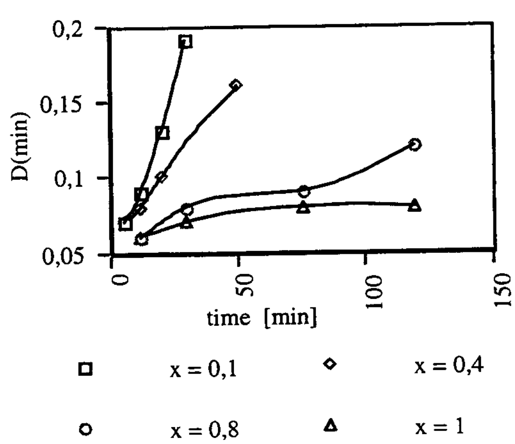

Figure 4: Fog D(min) of a photographic $AgBr_xCl_{1-x}$ emulsion (x = 0 ...1) as a function of S/Au sensitization according to fig. 3.

Sensitivity of the pure AgCl emulsion is low and increases with increasing content of bromide ions. Maximum sensitivity is reached at x(Br^-) = 0,9. As expected, the formation speed of sensitization centers as well as the fog D(min) decrease with decreasing content of chloride ions. Fig. 5 presents the rate constants k_1 for silver cluster formation from selected $AgBr_xCl_{1-x}$. Rate constants increase with increasing content of bromide ions within the crystals up to a value comparable to the optimum value of k_1 in the pure sulfur-sensitized AgBr emulsion, see fig. 2. The increase in k_1 is accompanied by an increase in [Ag_i^+] measured by dielectric loss spectroscopy.

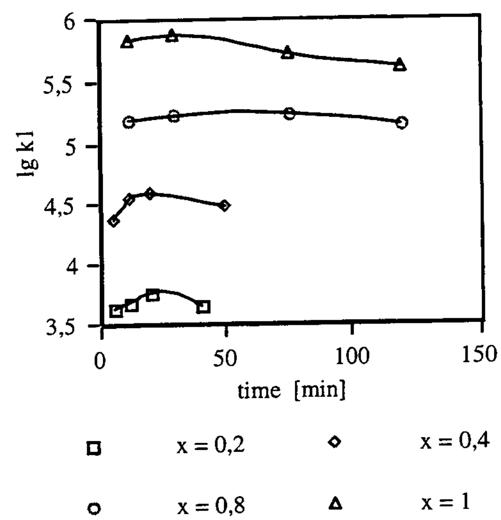

Figure 5: Rate constant k_1 from photo-emf traces of a photographic $AgBr_xCl_{1-x}$ emulsion (x = 0,2 ...1) as a function of S/Au sensitization according to fig. 3.

As a trend one can see again quite similar maximum times for the formation constants k_1 and sensitivity S(rel) at same mole fractions x(Br^-).

Conclusions

Pure AgBr and $AgBr_xCl_{1-x}$ model photographic emulsion (x = 0,2 ...1) show similar behavior in photo-emf measurements , if sulfur or combined sulfur / gold sensitization is used as method in increasing the sensitivity of these emulsions. $AgBr_{1-x}I_x$ (x = 0 .... 0,12) model emulsions for comparison show a somewhat different behavior. In the latter case differences will be discussed as the consequence of of the iodide content.

A comparison of two different kinetic models describing the photo-emf decay curves will be given.

References

1. W. JAHR, Ph.D. thesis, Univ. Halle-Wittenberg (1993)
2. J. HARENBURG, Diploma work, TH Merseburg (1991)