

Supersensitization of Photographic Emulsions by Rare Earth Ions: Luminescence Study

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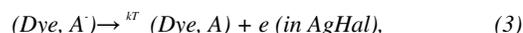
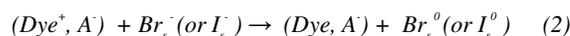
Abstract

Photographic and luminescence (77K) properties of spectrally sensitized AgBr and AgBr(I) emulsions were studied. Seven different cyanine dyes have been used for spectral sensitization in the visible and near infrared spectral ranges. Intrinsic and spectral sensitivity as a function of dye concentration (c) was measured. We observed the correlation between desensitization at $c > 10^{-4}$ mole Dye/mole AgBr and the shift of the reflectance spectrum to the red; both effects are due to formation of polymolecular form of dye. Addition of trivalent rare earth ions (REI^{3+}) to such emulsions completely eliminates desensitization (supersensitization effect). Moreover, the following changes in the luminescence are observed: the decrease of the adsorbed dye luminescence intensity; the increase of the intensity of the AgBr(I) green luminescence excited by the light with $\lambda < 460\text{nm}$; the dramatic drop in the intensity of the green anti-Stokes AgBr(I) luminescence, excited with the light from the dye absorption spectrum. Both photographic and luminescence changes occurring upon addition of REI^{3+} are explained by formation of $[Dye:REI^{3+}]$ complexes. Supersensitization in the presence of REI^{3+} is observed in gelatin emulsions, but not in polyvinyl alcohol ones. Such a difference is explained by formation of $[Gel:REI^{3+}]$ complexes adsorbed on the AgHal surface.

Introduction

The effect of trivalent rare earth ions (REI^{3+}) on spectral sensitization of silver halide emulsions was described previously [1]. In essence, the addition of REI^{3+} (Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tu^{3+} , Yb^{3+}) or their complexes with ethylenediaminetetraacetic acid ($[REI:EDTA]^{-1}$) into emulsion spectrally sensitized with anionic or cationic J-aggregating dyes affects its sensitivity. Dye concentration, microcrystal (MC) habitus, and the dye charge are all important factors. The sensitivity increase is observed only if an external complex between adsorbed dye and REI^{3+} or $[REI:EDTA]^{-1}$ is formed due to electrostatic interaction [2, 3]. When these complexes absorb light, an electron is transferred from an excited dye (Dye^*) to an

acceptor level (A) in the complex. It should be noted that REI^{3+} have many unoccupied sub-levels in the 4f shell that can serve as acceptors. The following thermal electron release from the acceptor level to the AgHal conduction band leads to latent image formation. These processes can be presented by the following reactions:



where Br_s^- (or I_s^-) are the surface anions, e is an electron in the AgHal conduction band, and kT denotes thermally activated process. Electron transfer from an excited dye to an acceptor level should result in the dye luminescence quenching as well as other changes of luminescence properties of the "MC-adsorbed dye" system. In the present paper we have chosen luminescence method to elucidate the effect of supersensitization in the presence of REI^{3+} . It should be noted that luminescence quenching of some organic molecules (e.g., dyes) in solution by REI^{3+} is well known (see, e.g. [4,5]).

Experimental

It has been shown previously (e.g., [6]) that the increase of spectral sensitizer concentration (c) in photographic emulsion causes sensitivity (S) decrease within the absorbance bands of both silver halide (desensitization) and dye (self-desensitization). Extensive studies were conducted to elucidate these effects and search for methods of their elimination or inhibition (supersensitization) [6-9].

To explain the mechanism of spectral sensitization in the presence of REI^{3+} we studied the sensitivity of AgBr photographic emulsions as a function of spectral sensitizer concentration. The AgBr emulsions were made by double-jet precipitation ($T=55^\circ\text{C}$, pH 6.0, pBr 3.0, the mean MC size $d=0.15\mu\text{m}$). Spectral sensitization was carried out by addition ($T=40^\circ\text{C}$) of various concentrations of one of the following dyes:

Dye I – 3,3'-di- γ -sulfopropyl-9-ethyl-4,5,4',5'-dibenzothiocarbocyanine betaine pyridinium salt ($E_{1/2\text{Red}} = -1.34\text{V}$, $E_{1/2\text{Ox}} = +0.67\text{V}$ relative to the saturated calomel electrode);

Dye II – 3,3'-di- γ -sulfopropyl-9-ethyl-5,5'-dimethoxythiocarbocyanine betaine pyridinium salt ($E_{1/2\text{Red}} = -1.32\text{V}$, $E_{1/2\text{Ox}} = +0.68\text{V}$);

Dye III – 1,1',3,3'-tetraethyl-5,5'-dicarboethoxyimidacarbocyanine iodide ($E_{1/2\text{Red}} = -1.55\text{V}$, $E_{1/2\text{Ox}} = +0.67\text{V}$);

Dye IV – 1,1',3,3'-triethyl-3'- γ -sulfopropyl-5,5'-dicarboethoxyimidacarbocyanine betaine ($E_{1/2\text{Red}} = -1.62\text{V}$, $E_{1/2\text{Ox}} = +0.63\text{V}$);

Dye V – 1,1',3,3'-tetraethyl-5,5',6,6'-tetrachloroimidacarbocyanine iodide ($E_{1/2\text{Red}} = -1.50\text{V}$, $E_{1/2\text{Ox}} = +0.58\text{V}$);

Dye VI – 3,3',9-triethyl-5,5'-dichlorothiocarbocyanine chloride ($E_{1/2\text{Red}} = -1.05\text{V}$, $E_{1/2\text{Ox}} = +0.94\text{V}$);

Dye VII – 3,3',9-triethyl-5,5'-diphenyloxycarbocyanine nitrate ($E_{1/2\text{Red}} = -1.33\text{V}$, $E_{1/2\text{Ox}} = +0.93\text{V}$).

Sensitivity of coated emulsions as a function of dye concentration is shown in Fig. 1: at $\lambda = 425\text{nm}$, in AgBr absorption band (curve 1), in the dye absorption band (curve 2), and at the peak position (λ_{max}) of the reflectivity spectrum of the emulsion (curve 3). The reflectance spectrum of coated emulsions comprises overlapping bands of dye molecules and aggregates in gelatin, as well as adsorbed on MC. It is important to note the correlation between sharp decrease in light sensitivity (desensitization and self-desensitization) and increase of λ_{max} (Fig.1). The long-wavelength shift of reflectance spectrum peak indicates that different polymolecular dye aggregates are formed (these are denoted here forth as Dye₁, Dye₂, Dye₃, etc.). These dye aggregates differ not only in their size, but also in their structure [10] when adsorbed on AgHal MC (e.g., see [6]). For some polymolecular forms of the examined dyes it is possible, first, to excite anti-Stokes luminescence of AgBr, AgBr(I) and AgI when light is absorbed by the dye adsorbed on MC [11], and, second, to create direct positive image in emulsions containing efficient electron traps [12]. These results imply that the increase of the number of molecules in dye aggregates brings down the electron energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the aggregate relative to energy bands of AgHal (Fig. 2a). In this case the absorption of light by Dye₂, Dye₃, etc. will create holes in the AgHal valence band, which, in turn, will lower the efficiency of latent image formation (self-desensitization). On the other hand, if light is absorbed by AgHal some of the aggregates can localize holes capable of recombining with photoelectrons, thus resulting in desensitization (the hole mechanism of desensitization). In the case of Dyes I-IV desensitization and self-desensitization is observed at $c > 10^{-3}$ mole Dye/mole AgBr.

Addition of REI^{3+} can eliminate desensitization and self-desensitization in absorption bands of some dye aggregates only if rare earth ion forms an external complex with adsorbed dye [1]. As an example, the data for Dye I

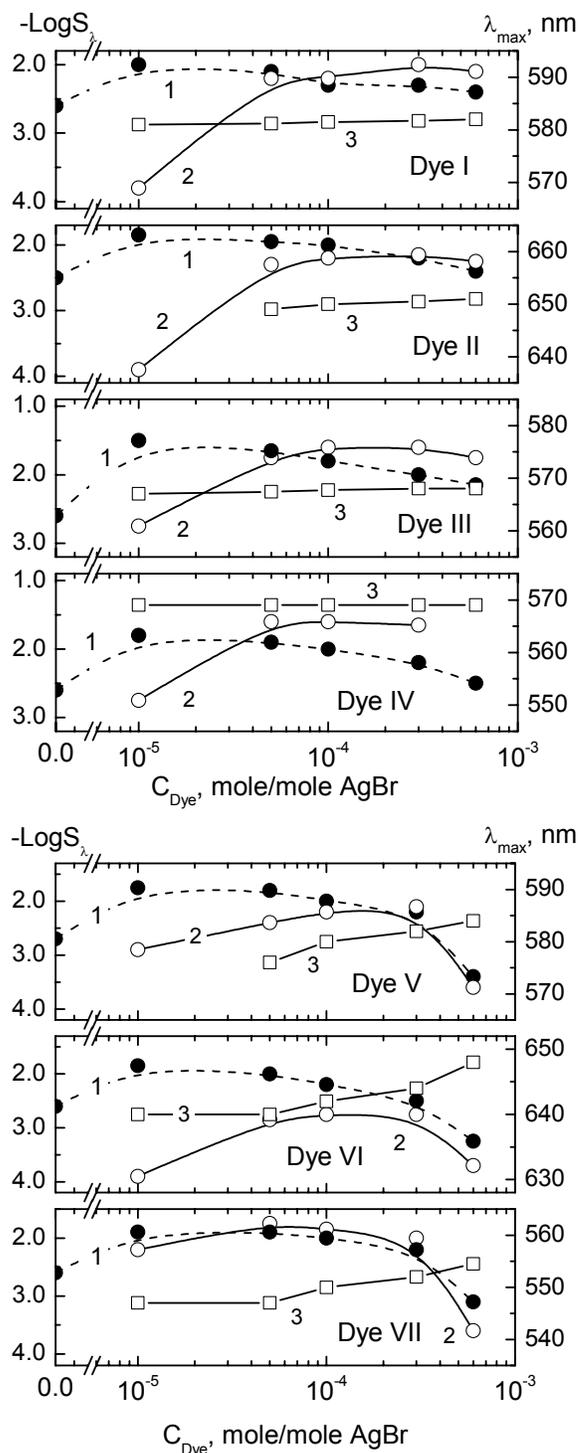


Figure 1. Sensitivity of coated emulsion as a function of dye concentration: 1 - within the fundamental absorption of AgBr ($\lambda = 425\text{nm}$); 2 - within the absorption band of dye; 3 - at the peak position of the reflectivity spectrum of this emulsion.

are shown in Fig. 3. As noted before [1], in the case of anionic Dye I, addition of REI^{3+} increases sensitivity

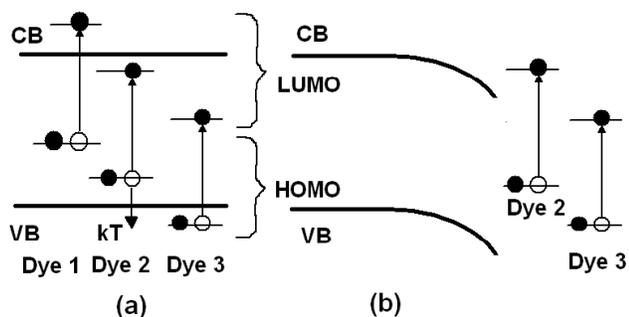


Figure 2. Schematic representation of the energy levels of different polymolecular forms of dye in reference to the conduction and valence bands of AgHal:

- (a) - no $[\text{Gel:REI}^{3+}]$ complexes on the surface of AgHal MC;
 (b) - $[\text{Gel:REI}^{3+}]$ complexes are adsorbed on the surface of AgHal MC.

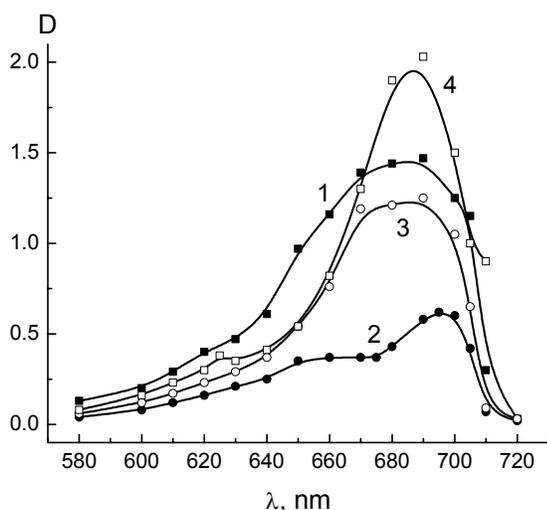


Figure 3. Optical density spectra of developed coated emulsions with various concentrations of Dye 1 (c) and Yb^{3+} (c_1). 1 - $c = 10^{-3}$ mole dye/mole AgBr; $c_1 = 0$; 2 - $c = 5 \times 10^{-3}$ mole dye/mole AgBr; $c_1 = 0$; 3 - $c = 5 \times 10^{-3}$ mole dye/mole AgBr; $c_1 = 5 \times 10^{-4}$ mole YbCl_3 /mole AgBr; 4 - $c = 5 \times 10^{-3}$ mole dye/mole AgBr; $c_1 = 10^{-3}$ mole YbCl_3 /mole AgBr.

The layers were exposed identically in a tungsten lamp

(supersensitization) only in the longest wavelength bands of dye aggregates, and does not eliminate self-desensitization in M- and J_1 -bands. As explained in [1], for $[\text{Dye:REI}^{3+}]$ complex to be formed, a specific structure of a dye adsorbed on MC is necessary.

As follows from our experimental data, supersensitization effect upon addition of REI^{3+} is observed only when gelatin and not polyvinyl alcohol (PVA) was used in emulsion synthesis (Fig. 4). It could be due to the fact that positively charged $[\text{Gel:REI}^{3+}]$ complexes adsorbed on MC cause downward bending of AgHal energy bands (a similar energy band bending occurs when the silver ion concentration on MC surface increases). If such bending takes place, first, the electron transfer from excited levels of

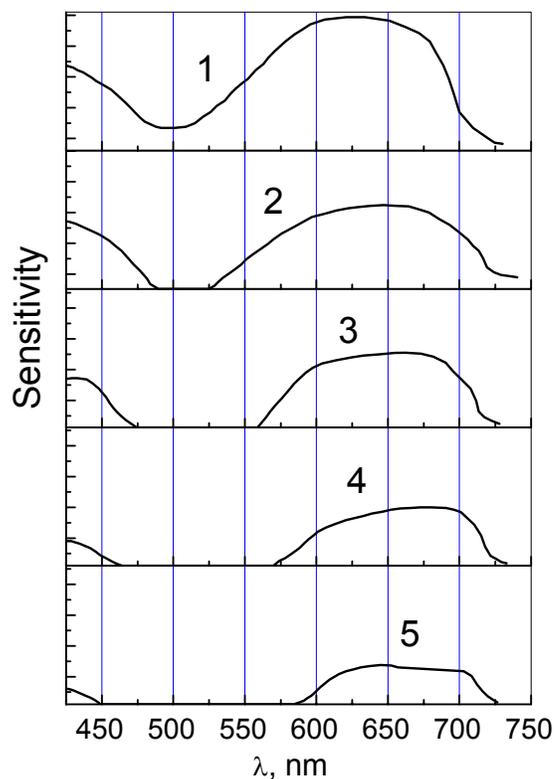


Figure 4. Reproduction of photographic wedge spectrograms from spectral sensitization of PVA AgBr emulsions with Dye 1 (4×10^{-4} mole dye/mole AgBr): 1 - no REI^{3+} ; 2 - Eu^{3+} (10^{-4} mole EuCl_3 /mole AgBr); 3 - Eu^{3+} (4×10^{-4} mole EuCl_3 /mole AgBr); 4 - $[\text{Eu}(\text{EDTA})]^-$ (10^{-4} mole/mole AgBr); 5 - $[\text{Eu}(\text{EDTA})]^-$ (4×10^{-4} mole/mole AgBr). The layers were exposed identically in a tungsten lamp spectrograph.

dye aggregates to AgHal conduction band is facilitated, and second, the efficiency of hole generation in the AgHal valence band upon light absorption by dye aggregates drops dramatically (Fig. 2b). Furthermore, the presence of positively charged $[\text{Dye:REI}^{3+}]$ or $[\text{Dye:(GelREI}^{3+})]$ complexes [1] rules out localization of photoholes by a dye.

Thus, our experimental data indicate that in the presence of REI^{3+} a number of processes could cause supersensitization. The most important of them are:

1. formation of $[\text{Dye:REI}^{3+}]$ or $[\text{Dye:(GelREI}^{3+})]$ complexes and proceeding of reaction (1);
2. positively charged $[\text{Dye:REI}^{3+}]$ or $[\text{Dye:(GelREI}^{3+})]$ complexes do not localize holes, and desensitization by the hole mechanism does not take place;
3. downward bending of the AgHal energy bands due to adsorption of positively charged $[\text{Gel:REI}^{3+}]$ complexes on MC; these complexes create shallow electron traps.

Desensitization of PVA emulsions (Fig. 4) occurs due to (i) formation of deep electron traps after adsorption of REI^{3+} on MC [1]; (ii) increased upward bending of the AgBr bands after adsorption of $[\text{REI:EDTA}]^-$ on MC; (iii) decreasing concentration of surface Ag^+ ions as a result of formation of $[\text{REI:EDTA}]^- \text{Ag}^+$ - complexes.

All above processes taking place at room temperature should also influence AgHal luminescence observed at low temperature ($T=77\text{K}$). It is quite obvious that if a dye no longer localize photoholes due to formation of $[\text{Dye:REI}^{3+}]$, they will be redirected and localized by "iodine centers" in AgBr(I). This, in turn, results in AgBr(I) luminescence intensity increase (iodine ions in AgBr(I) give rise to green luminescence). Furthermore, reaction (1) should bring about the quenching of adsorbed dye luminescence, and the absence of holes in the AgBr valence band due to

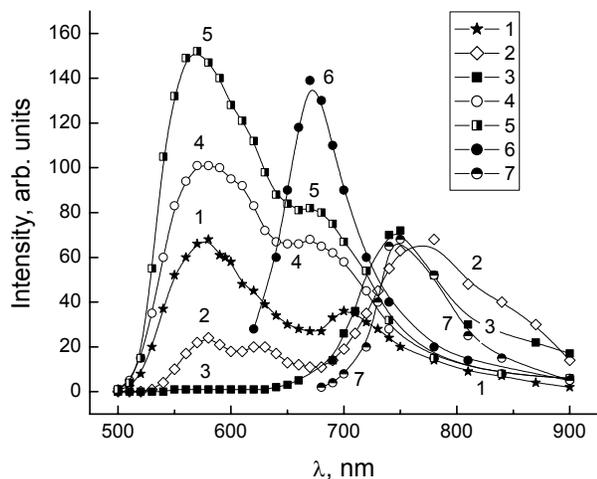


Figure 5. Phosphorescence spectra of AgBr(I) emulsions excited with $\lambda_{\text{ex}} = 450\text{nm}$ (curves: 1,4,5) and $\lambda_{\text{ex}} = 650\text{nm}$ (2,3) without REI^{3+} (1,2) and with Eu^{3+} (3), Yb^{3+} (4), and Nd^{3+} (5). REI^{3+} concentration is 10^{-3} mole REI^{3+} /mole AgBr. Curves 6 and 7 are fluorescence and phosphorescence of Dye in gelatin, respectively.

downward energy band bending (Fig. 2b) causes sharp decrease of anti-Stokes AgHal luminescence (in particular, green AgBr(I) luminescence) when light is absorbed by adsorbed dye.

The above conclusions completely agree with our experimental data. As an example, luminescence of AgBr(I) emulsion with added Dye I is shown in Fig. 5. AgBr(I) emulsion (3mol% AgI) was made by double-jet precipitation at pBr 3.0, $T=55^\circ\text{C}$, pH 6.0, ($d=0.15\mu\text{m}$). In the absence of REI^{3+} phosphorescence spectrum (excited with $\lambda_{\text{ex}} = 450\text{nm}$) consists of two overlapping bands – the iodine center green peak and the delayed fluorescence band with $\lambda_{\text{max}} = 700\text{nm}$ due to adsorbed dye (Fig. 5, curve 1) [11]. When light is absorbed by the dye adsorbed on MC ($\lambda_{\text{ex}} = 650\text{nm}$), both the AgBr(I) anti-Stokes phosphorescence and dye phosphorescence ($\lambda_{\text{max}} = 770\text{nm}$) are detected (Fig. 5, curve 2). After addition of REI^{3+} dye luminescence ($\lambda_{\text{max}} = 700\text{nm}$ and 770nm) drops dramatically, green AgBr(I) luminescence increases (Fig. 5, curves 4,5), and anti-Stokes luminescence is not detected (Fig. 5, curve 3). The only luminescence bands ($\lambda > 650\text{nm}$) recorded in the presence of REI^{3+} are due to the dye suspended in gelatin.

Conclusions

Our results confirm proposed supersensitization mechanism of photographic emulsions in the presence of REI^{3+} . This mechanism differs entirely from other methods of supersensitization described previously [6-9]. The downward bending of the AgHal energy bands facilitates spectral sensitization by infra-dyes. Thus, as expected from the proposed mechanism, addition of REI^{3+} to photographic emulsion with infra-dyes brings about the effect of supersensitization.

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Biography

Alexander Yu. Akhmerov graduated from Odessa National University, Ukraine in 1975. He received his Ph.D. in 1989 in Optics and Photographic Materials from Odessa National University, Ukraine. He has worked in Research Institute of Physics of Odessa National University of Ukraine since 1975.