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Review of Luminescence Studies of Mechanisms of Spectral Sensitization and Supersensitization: Chemically Sensitized Emulsions

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The sulfur sensitization of photographic emulsions leads to the formation of silver sulfide clusters on the surface of emulsion microcrystals (MC). The size of the clusters is between 3 and 10 nm. The clusters of small size $(Ag_2S)_n$ are hole traps, the mixed clusters $(Ag_2S)_pAg_k^+$ ($k < m = 4$) are the sensitivity centers, but larger clusters $(Ag_2S)_pAg_m^+$ ($m \geq 4$) are the fog or latent image centers. In addition, emulsion dye can be adsorbed not only by AgBr MC but also by the silver sulfide clusters. We have shown that light absorption by dye can give rise to the cluster luminescence and, vice versa, the light absorption by the clusters can excite the luminescence of adsorbed dye. We also have shown that when a TAI layer is formed between clusters and adsorbed dye, the dye luminescence disappears if light is absorbed by the cluster. These results prove that in the presence of the TAI layer the relocalization of charge carriers from the excited levels of clusters to dye is impossible. Thus, at room temperature, the TAI layer can inhibit the process of desensitization of Type I, and therefore, TAI works as supersensitizer. We have also established, using luminescence studies, the important role of the surface anions of the emulsion MC in the mechanism of spectral sensitization.

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Introduction

Studies of low-temperature luminescence of silver halide microcrystals (MC) with adsorbed dyes are important for understanding mechanisms of spectral sensitization of silver halide emulsions. Using the luminescence method, not only is it possible to investigate the processes in the excited molecules and aggregates, it is also possible to determine electron and hole exchange reactions between excited or ionized dye and silver halide that are responsible for spectral sensitization.[1,2]

The following important results have been described previously:

- Specific features of luminescence spectra of adsorbed dye molecules and aggregates.[3–5]
- Influence of dye adsorption on silver halide luminescence.[6,7]
- Appearance of silver halide anti-Stokes luminescence when the light is absorbed by adsorbed dye.[8–13]
- Fluorescence lifetimes for dye adsorbed on silver halide microcrystals.[14–17]
- Energy level position of the dye relative to silver halide energy bands.[18,19]

The photoluminescence method has also been used to substantiate a mechanism of supersensitization, which is a process involving the relocalization of a hole from sensitizer to the supersensitizer.[20–22] In the 1990s, the low-temperature fluorescence of different, separate J-aggregates of the dye adsorbed on the silver halide surface has been observed directly with the help of luminescent[23] or electron[24] microscopes.

Most of the experimental data were obtained for dye adsorption on the silver halide MC free from chemical sensitization. However, for a vast number of applications, the investigation of spectral sensitization processes in chemically sensitized emulsions is more important. Many published reports discuss the interaction of chemical and spectral sensitization of silver halide emulsions.[25–32] The present article is devoted to the comparison of luminescence and photographic properties of AgBr emulsions subject to both chemical (sulfur or reduction) and spectral sensitization.

Previously, it has been determined[33–37] that sulfur sensitization leads to the formation of silver sulfide clusters on the surface of silver halide emulsion MC. Silver sulfide clusters create a system of occupied energy levels above the top of the AgBr valence band, so that these clusters cause luminescence in the near-infrared region.[33–37] The spectral peak position of this emission depends on the size of the clusters.[36,38] Such a variation is a dimensional effect in the luminescence from the narrow-band Ag_2S semiconductor. Mixed clusters of $(Ag_2S)_pAg_m^+$ ($m \geq 4$) type are the fog or latent image centers,[39,40] while clusters of $(Ag_2S)_pAg_k^+$ ($k < m$) type are sensitivity centers.[40,41] The developing capacity of the $(Ag_2S)_pAg_m^+$ clusters depends on the silver fragment size; therefore, the breakdown of the silver fragment by holes in the mixed clusters is the basis of direct positive image formation. According to luminescent studies as well as electron microscopy data,[38] the diameter (d) of $(Ag_2S)_p$ clusters is less than 15 nm and lies in the region from 3 to 7 nm. Furthermore, it is well known[42] that an area occupied by one molecule of sensitizer on the surface of MC is less than 1 nm^2, which is significantly smaller than the surface area of $(Ag_2S)_p$ clusters. Thus, in the case of sulfur sensitized emulsions it is imperative to consider the adsorption of spectral sensitizers not only on AgBr but also on the silver sulfide clusters or ac-

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count for the possibility of the contact between the molecule (aggregate) of spectral sensitizer adsorbed on AgBr and the impurity cluster. This situation has not been discussed earlier,[2,43,44] so the following important processes for spectral sensitization have not been discovered:

- Interaction of the excited dye adsorbed on the cluster with silver sulfide clusters.
- Interaction of excited or ionized clusters with the adsorbed dye.

We shall show that the interaction processes suggested above can be confirmed by the luminescent method (see also Refs. 45 through 51).

The $(Ag_2S)_n$ and $(Ag_2S)_pAg_k^+$ $(p > n)$ cluster formation on sulfur sensitization occurs as a result of the interaction of sulfur sensitizer with the surface silver ions of emulsion MC. Cluster formation leads to the increase in the concentration of defects in the subsurface layer of MC and, as a result, to the increase in the concentrations of Br_s^- and I_s^- surface anions.[41] (The uncontrolled iodide impurities are always present in AgBr.) Similar processes also occur in the case of silver center formation during reduction sensitization.[41] The increase of the defect concentration in the subsurface layer of the emulsion MC during chemical sensitization also promotes migration processes and the appearance of paired iodine centers $I_s^-I_s^-$, even in AgBr MC. The surface anions, Br_s^-, I_s^-, and $I_s^-I_s^-$ form local energy levels above the valence band of AgBr.[41,52,53] These anions can take part in the regeneration of photogenerated radical cations (Dye^+) of the dye[54]:

$$Dye^+ + Br_s^- \ (I_s^- \text{ or } I_s^- \ I_s^-) \Rightarrow Dye + Br_s^0 \ (\ I_s^0 \text{ or } I_s^0 \ I_s^-) \quad (1)$$

or reduce excited (Dye^*) dye with anion radical Dye^- formation as a result[25,55]

$$Dye^* + Br_s^- \ (I_s^- \text{ or } I_s^- \ I_s^-) \Rightarrow Dye^- + Br_s^0 \ (I_s^0 \text{ or } I_s^0 \ I_s^-). \quad (2)$$

The I_s^- anions are responsible for the orange luminescence of AgBr at low temperature (T = 77 K)[41,53,56] while $I_s^-I_s^-$ pair centers determine the green luminescence of AgBr(I) MC.[57,58] The existence of these luminescent bands is the result of radiative recombination in donor–acceptor pairs (DAP)[41,53]:

$$AgBr + h\nu_{ex} \Rightarrow e + h, \quad (3)$$

$$(Br_s^- \ I_s^- \ ... \ Ag_s^+) + e + h \Rightarrow (Br_s^- \ I_s^0 \ ... \ Ag_s^0) \Rightarrow (Br_s^- \ I_s^- \ ... \ Ag_s^+) + h\nu_{lum} \ (2.0 \text{ eV}), \quad (4)$$

$$(I_s^- \ I_s^- \ ... \ Ag_s^+) + e + h \Rightarrow (I_s^- \ I_s^0 \ ... \ Ag_s^0) \Rightarrow (I_s^- \ I_s^- \ ... \ Ag_s^+) + h\nu_{lum} \ (\sim 2.17 \text{ eV}), \quad (5)$$

where Br_s^-, I_s^- , and Ag_s^+ are surface ions.

The orange emission of AgBr MC can also appear as a result of direct ionization of Br_s^- (excitation band with λ_{max} = 470 nm) followed by tunnel relocalization of the hole ($Br_s^0 \Rightarrow I_s^-$) or direct ionization of I_s^- (excitation band with λ_{max} = 490 nm).[41] Let us define the excitation efficiency of orange emission of AgBr MC in the bands with λ_{max} = 470 and 490 nm as η_{470} and η_{490}, respectively. It was shown[41] that in the primary stage of both sulfur and reduction sensitization, these values increase with the duration (t_2) of sensitization or ripening. Quantities η_{470} and η_{490} pass through the maximum before the sensitivity (S) taken as a function of t_2 does. The increase of η_{470} and η_{490} values can be explained by the increase of the concentration of Br_s^- and I_s^- ions that are the members of the donor–acceptor pairs. Such a change is explained by the fact that at the sulfur and reduction sensitization surface, as well as subsurface, silver cations are used for impurity cluster formation.[41] The formation of impurity centers of sensitivity and fog that function as electron traps [e.g., clusters of $(Ag_2S)_p$ Ag_k^+ (k = 1,2...m) type[41]] during the later stages of sensitization results in the decrease of η_{470} and η_{490} values. It is clear now that comparison of experimental $\eta_{470} = f(t_2)$ and $\eta_{490} = f(t_2)$ functions with the $S_\lambda = f(t_2)$ function (at T = 300 K) in the case of AgBr emulsion during chemical and spectral sensitization (here S_λ is the sensitivity in the absorption bands of the dye) can help to establish the role of Br_s^- and I_s^- anions in the spectral sensitization process by the dyes adsorbed directly on the AgBr surface modified by chemical sensitization.

Luminescence Properties of the System, Silver Sulfide Cluster with Adsorbed Dye

Silver sulfide clusters are formed both on the surface of emulsion AgBr MC as a result of sulfur sensitization with sodium thiosulfate, and in a solution of inert gelatin according to the technique described previously.[37,38] Low-temperature (T = 77 K) luminescence of these clusters was observed in the near-infrared spectral region (λ = 800 to 920 nm). The following dyes additionally introduced after sulfur sensitization of emulsion were used as spectral sensitizers:

I. 1,1′-diethyl-2,2′-quinocyanineiodide (the redox potential $E_{1/2 \text{ Red}} = -1.15$ V, the oxidation potential $E_{1/2 \text{ Ox}} = +0.90$ V relative to the saturated calomel electrode).
II. 1,1,3′-di-triethyl-3-g-sulfopropyl-5,5′-dicarboethoxy-imidacarbocyanine betaine ($E_{1/2 \text{ Red}} = -1.62$ V, $E_{1/2 \text{ Ox}} = +0.53$ V);
III. 3,3′,9-triethyl-5,5′-diphenyloxacarbocyanine nitrate ($E_{1/2 \text{ Red}} = -1.28$ V, $E_{1/2 \text{ Ox}} = +0.96$ V).

The same dyes were added into the inert gelatin solution containing the silver sulfide clusters. All dyes were selected in such a way that their absorption bands overlapped with the absorption bands of the silver sulfide clusters (spectral region[36] from 500 to 700 nm), but the dye luminescence did not fall in the region of IR luminescence of the clusters. Spectral dependencies of the reflection coefficient (T), the optical density (D), and absorption coefficient (A, %) were measured at T = 300 K using the integrating sphere. All luminescence measurements for all samples were done at T = 77 K.

Figure 1 shows excitation spectra of luminescence (a) and the dependence $D = f(\lambda)$ and (b) for gelatin layers containing silver sulfide clusters (the emission band of clusters at λ_{max} = 920 nm) and Dye I at different concentrations. In the case of small dye concentrations (C) [Fig. 1(a), Curves 2 through 4], decrease was observed of the excitation efficiency (η) for luminescence of clusters in M-(λ_{max} = 530 nm) and J-(λ_{max} = 570 nm) absorption bands of the dye. The increase of dye concentration gives rise to the typical dye sensitized luminescence of the clusters with maxima in $\eta = f(\lambda)$, at 530 and 570 nm [Fig. 1(a), Curves 5 and 6]. The control experiments showed that the decrease of η [Fig. 1(a), Curves 2 through 4] was not associated with light absorption by the fraction of the dye in the gelatin layer that was not adsorbed on the clusters. (More detailed discussion can be found in Refs. 46 and 49.) Therefore, the decrease of η in the regions of M- and J-absorption bands of the dye is explained by the antiresonance effect described by Fano.[59]

In his work, Fano showed, on the basis of quantum mechanical principles, that if excited states of an atom

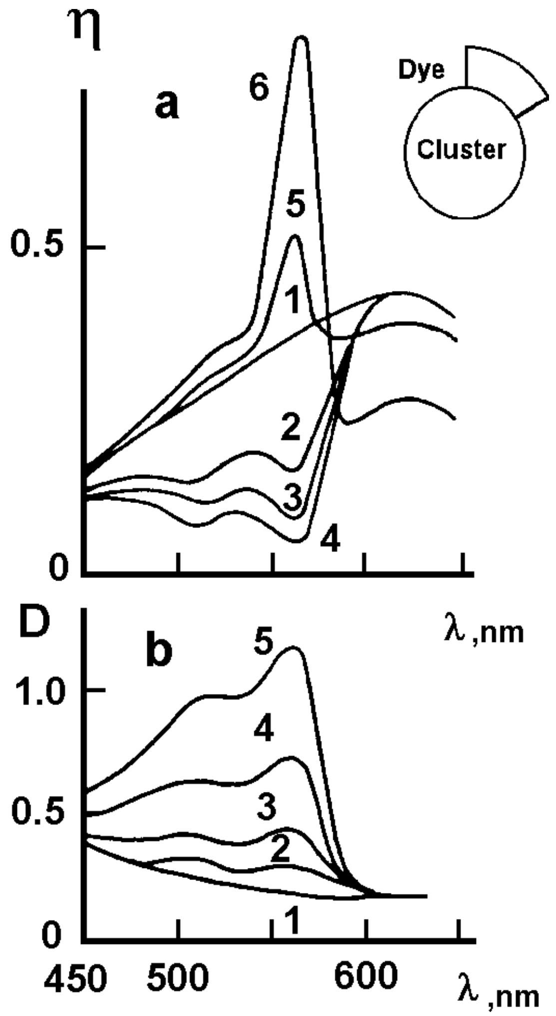

Figure 1. (a) Infrared luminescence excitation spectra of gelatin layers containing silver sulfide clusters (emission band of clusters with λ_{max} = 920 nm) and the following concentrations of Dye I (10^{-4} M): (1) 0.0, (2) 0.25, (3) 0.5, (4) 1.0, (5) 5.0, (6) 10.0. Value η is given in arbitrary units. (b) Absorption spectra for the same gelatin layers.

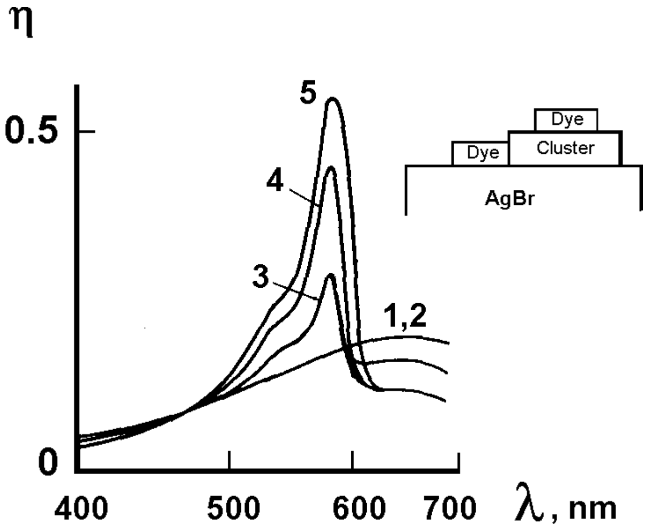

Figure 2. Infrared luminescence excitation spectra of sulfur sensitized AgBr emulsion (silver sulfur cluster emission band with λ_{max} = 890 nm) with different concentrations (mol Dye I/mol AgBr) of added Dye I: (1) 0.0, (2) 10^{-6}, (3) 10^{-4}, (4) 5×10^{-4}, (5) 10^{-3}. Value η is given in the arbitrary units.

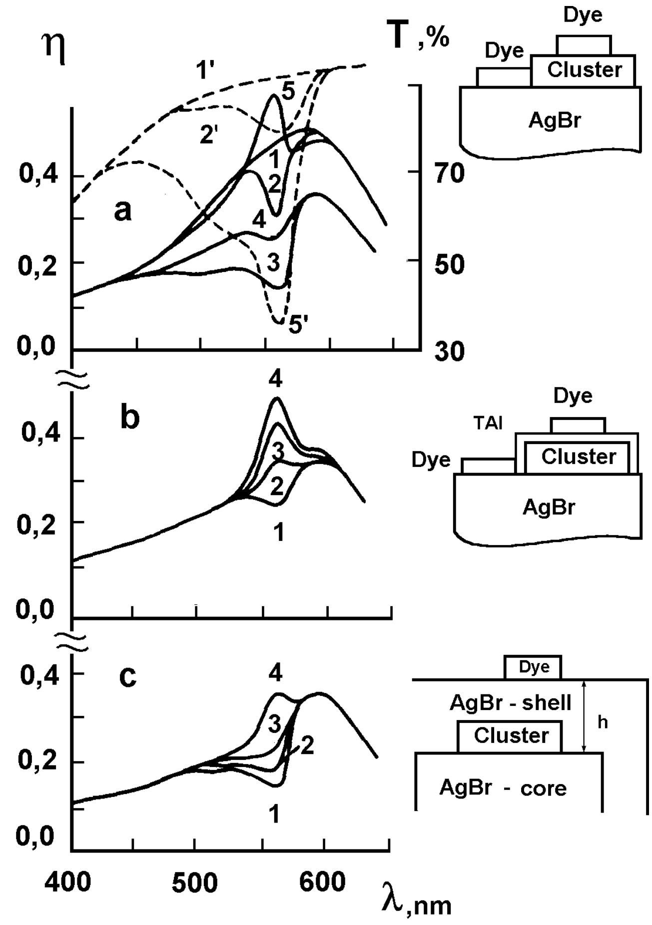

Figure 3. (a) Infrared luminescence excitation spectra (solid Curves 1 through 5) and spectra of the reflection coefficient (dashed curves 1′ through 5′) for layers of sulfur sensitized emulsion (emission band for clusters λ_{max} =800 nm) with added Dye II in different concentrations (10^{-4} mol/mol AgBr): 1,1′—without Dye; 2,2′—0. 1; 3—0. 6; 4—1. 0; 5,5′—6. 0. (b) Infrared luminescence excitation spectra of sulfur sensitized AgBr emulsion containing 10^{-4} mol Dye II/mol AgBr and following concentrations (gram/Liter) of TAI: 1—0.0 (without TAI); 2—0.1; 3—0.3; 4—0.8. (c) Infrared luminescence excitation spectra of sulfur sensitized AgBr emulsion containing 6×10^{-5} mol Dye II/mol AgBr. Emulsion microcrystals were covered by AgBr shells with the following thicknesses (Å): 1—0.0; 2—10.0; 3—15.0; 4—20.0. The functions $\eta = f(\lambda)$ have been normalized for their values at λ = 400 nm. Value η is given in arbitrary units.

or a molecule overlap with the continuum of the energy levels of another system and, in addition, there is an interaction between the excited states and the continuum, the distinctive, so called “hole burning” can be observed in the absorption spectra. The appearance of such “hole burning” in the absorption spectra of the systems under discussion is called antiresonance effect. It is important to note (see Ref. 59), that, first, “hole burning” in the absorption spectra is observed at wavelengths that correspond to the absorption bands of the atoms or the molecules; and, second, only in the case of direct contact between these atoms (molecules) and the system with the continuum energy spectra can antiresonance be observed.

Accordingly, in the “cluster–adsorbed dye” systems, the decrease of excitation efficiency of the cluster luminescence in the spectral region where dye absorbs [see

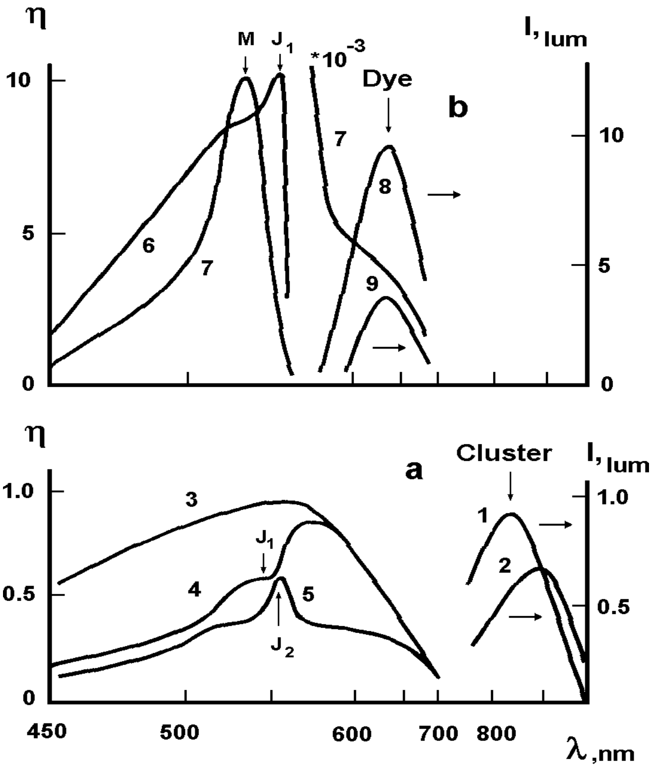

Figure 4. (a) Curves 1 and 2 are luminescence spectra of the silver sulfur clusters under excitation with light with λ = 615 nm (1) and λ = 690 nm (2). Curves 3 through 5 are infrared luminescence excitation spectra of the silver sulfur clusters in sulfur sensitized emulsion without Dye III (Curve 3) and with Dye III in concentrations (mol dye/mol AgBr): 5×10^{-5} (Curve 4) and 3×10^{-4} (Curve 5). (b) Fluorescence excitation spectra of J-aggregates of Dye III (Curve 6) and phosphorescence excitation spectra of Dye III molecules (Curve 7). Curves 8 and 9 are phosphorescence spectra for Dye III under excitation with light of λ = 530 nm (Curve 8) and λ = 690 nm (Curve 9). Value η is given in arbitrary units.

Figs. 1(a), Curves 2 through 4 and Fig. 1(b)] is due to the antiresonance effect.[46,47]

Results described for gelatin layers were also observed in the case of sulfur sensitized AgBr emulsions with added spectral sensitizers I through III. The excitation spectra of IR luminescence of silver sulfide clusters in sulfur sensitized emulsions with Dye II and Dye III display the "hole burning" [Fig. 3(a), Curves 2 through 4 and Fig. 4(a), Curve 4] caused by the antiresonance effect. In addition, it is essential that the increase of η in the spectral region where dye absorbs was observed only at relatively high concentrations of dye [Figs. 2; 3(a), Curve 5; and 4(a), Curve 5]. In this case the polymolecular layer of dye is formed on the cluster. In the excitation spectra of the system "cluster–adsorbed dye II" the antiresonance effect is observed in the M- and J_1-bands, but increase of η is observed in the J_2-band [Fig. 4(a), Curves 4 and 5]. Here, the notations J_1 and J_2 for aggregates were borrowed from Ref. 60. Therefore, it is possible to conclude that layer-by-layer adsorption of dye on the clusters promotes the J_2-aggregate formation.

Figure 5 schematically shows the energy levels for the silver sulfide clusters and the energy levels of the molecules and the aggregates of adsorbed dye in contact (Dye_1) or not in contact (Dye_2) with the cluster. This energy diagram is an example of when the excited energy level of dye (S_1) is located below the bottom of the AgBr conduction band. Dye_1 does not absorb light because of antiresonance [Fig. 5(a)]. Therefore, the cluster luminescence (Lum) sensitized by dye appears only under conditions of light absorption (Abs) by Dye_2 with further relocalization of an electron and a hole from excited Dye_2 to the cluster. [These electronic transitions are shown in Fig. 5(b) by arrows]. For dye adsorbed on the surface of the emulsion MC that are in direct contact with the cluster, the electron relocalization from exited Dye_2 probably occurs in two stages. First, the electron appears in the conduction band of AgBr and then on the excited states of the cluster. At the same time, the hole

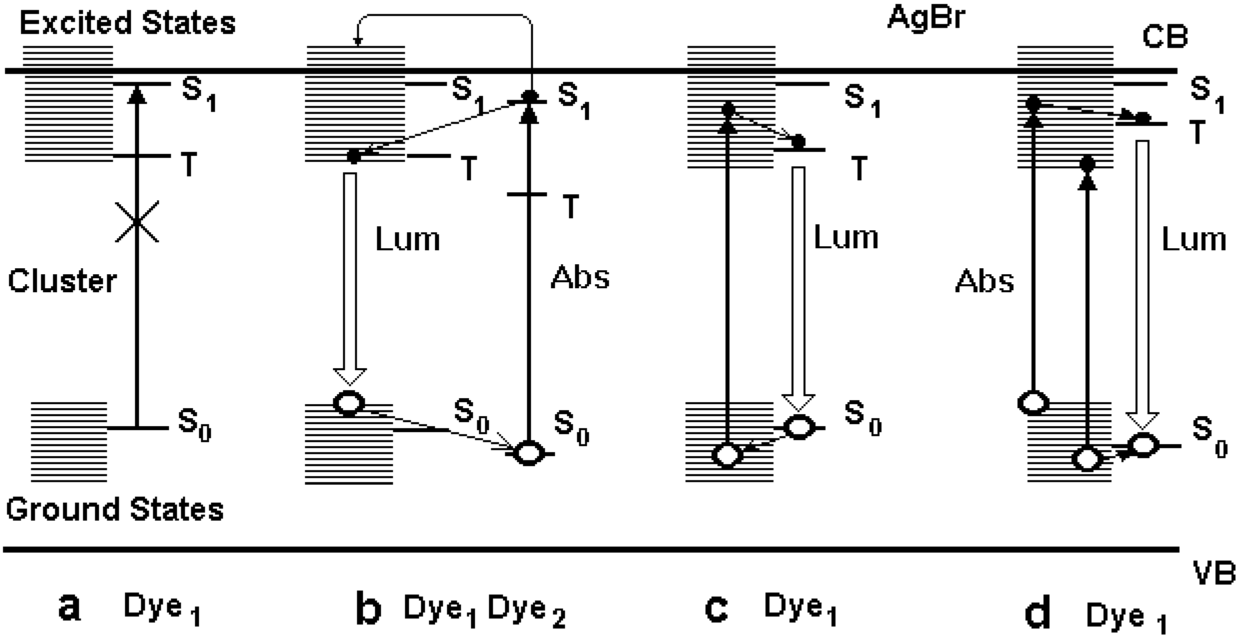

Figure 5. The energy level scheme for the silver sulfur clusters with adsorbed dye. The levels are shown relative to AgBr energy bands: CB is the AgBr conduction band; VB is the AgBr valence band; S_0, S_1 are the singlet levels; and T is the triplet level of dye. (Shown is a specific case of dye with S_1 level below the bottom of the AgBr CB.)

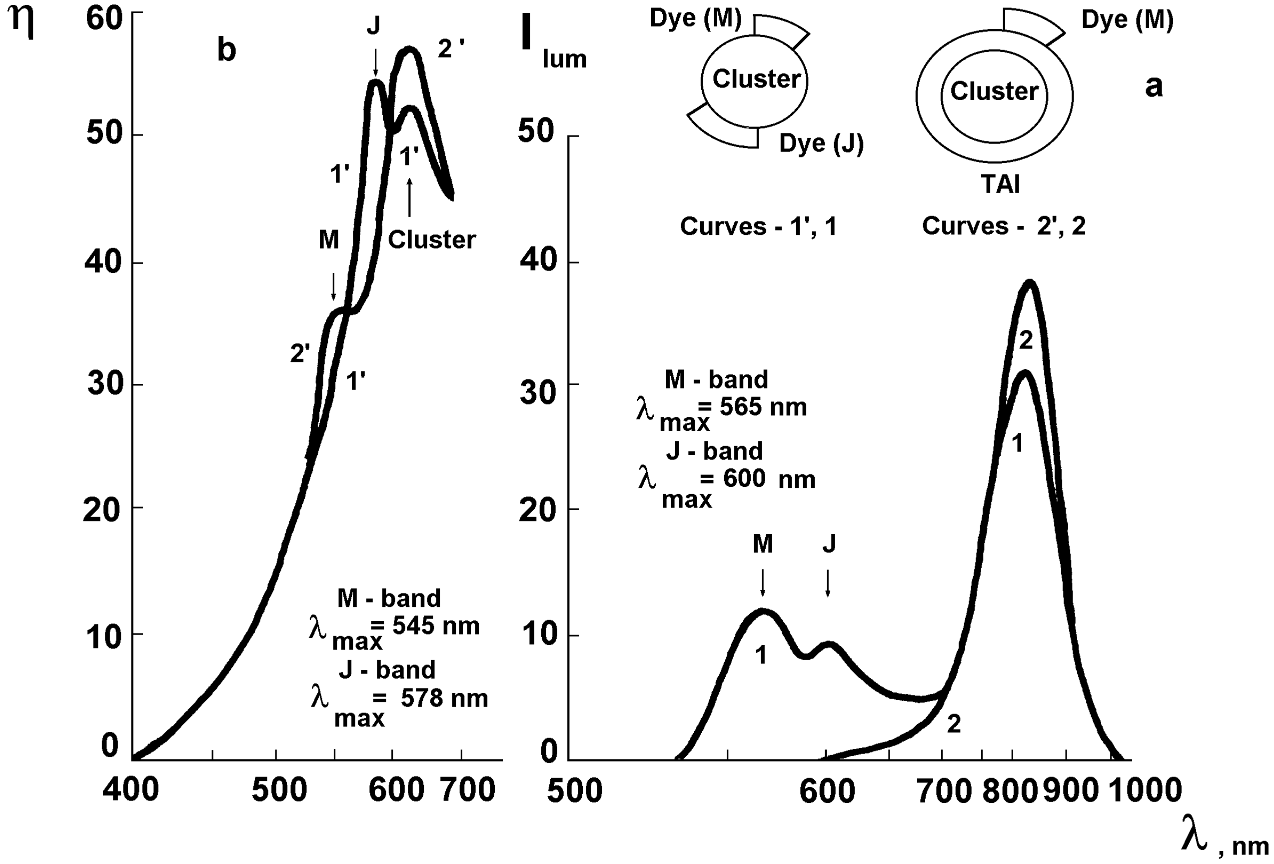

Figure 6. Low-temperature (T = 77 K) luminescence spectra (a) (Curves 1 and 2) and infrared luminescence excitation spectra (emission band with λ_{max} = 840 nm) (b) (Curves 1′ and 2′) of cooled 5% gelatin solutions containing the silver sulfur clusters (full concentration 5 × 10^{-3} M) and Dye I (10^{-4} M) (Curve 1, 1′), and the silver sulfur clusters, TAI (0.02 g/L) and Dye I (Curves 2, 2′). Values I_{lum} and η are given in arbitrary units.

relocalizes from ionized Dye$_2^+$ into the system of the cluster ground states. Indicated relocalization of charge carriers results in cluster luminescence [Fig. 5(b)].

In the presence of the polymolecular layer of dye on the surface of the cluster, not only can dye sensitized luminescence of the cluster be observed, but also two interconnected effects can occur[50,51]:

- Decrease of the excitation efficiency of the cluster luminescence in the spectral region where dye does not absorb, i.e., at $\lambda > \lambda_{max}$, where λ_{max} is the wavelength corresponding to the maximum of the function $\eta = f(\lambda)$ [see Fig. 1(a), Curves 5 and 6; Fig. 2, Curves 3 through 5; Fig. 3, Curves 3 through 5; and Fig. 4(a), Curve 5].
- Excitation of dye phosphorescence in the spectral region $\lambda > \lambda_{max}$ [Fig. 4(b), Curve 7].

These effects are induced by hole and electron relocalizations from the excited cluster onto the ground and triplet levels of the dye, respectively [see Fig. 5(c)]. These data confirm that in the system “cluster–adsorbed dye”, depending on the photon energy used for excitation, charge carrier relocalization is possible from dye to cluster and vice versa.[50,51] Awareness of this property of the system is essential for a better understanding of the spectral sensitization process; it can also be useful in molecular electronics.

The wide system of energy levels of ground and excited states in the cluster allows the inducement of the anti-Stokes dye phosphorescence on two photon excitation of the cluster. [These electronic transitions are shown in Fig. 5(d)]. For Dye III such results are shown in Fig. 4(b), Curve 9. In this case, the dye phosphorescence is excited[50,51] by monochromatic light with λ = 690 nm.[50,51]

A necessary condition for antiresonance is not only the energetic correspondence of the excited states of dye and the cluster, but also the direct contact of the cluster and dye. Thus, the suggested antiresonance effect in the system “cluster–adsorbed dye” undoubtedly proves dye adsorption on the cluster. If a monomolecular “insulating” layer of another substance is created between the cluster and dye or the cluster and dye are separated by the silver halide layer (MC of “core–shell” type), the conditions for antiresonance will vanish. As expected in this case, the weakening of antisensitization effect due to antiresonance is observed [Figs. 3(b), 3(c) and Fig. 6].[48,49] As an “insulating” layer we have used a well-known stabilizer: 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI). This substance (which in some earlier papers is called “sta-salt”) has preferential adsorption on silver sulfide compared to silver halide.[61] At TAI concentrations exceeding 0.1 g/L, first, only a typical case of dye sensitized luminescence of the cluster is recorded, and, second, the excitation efficiency of the cluster luminescence increases at $\lambda > \lambda_{max}$ where dye does not absorb [Figs. 3(b), and 6].

Luminescence studies of the system “silver sulfide cluster–TAI layer–adsorbed dye” provide a possibility to discover the electron relocalization process from the excited levels of cluster not only to the triplet, but also

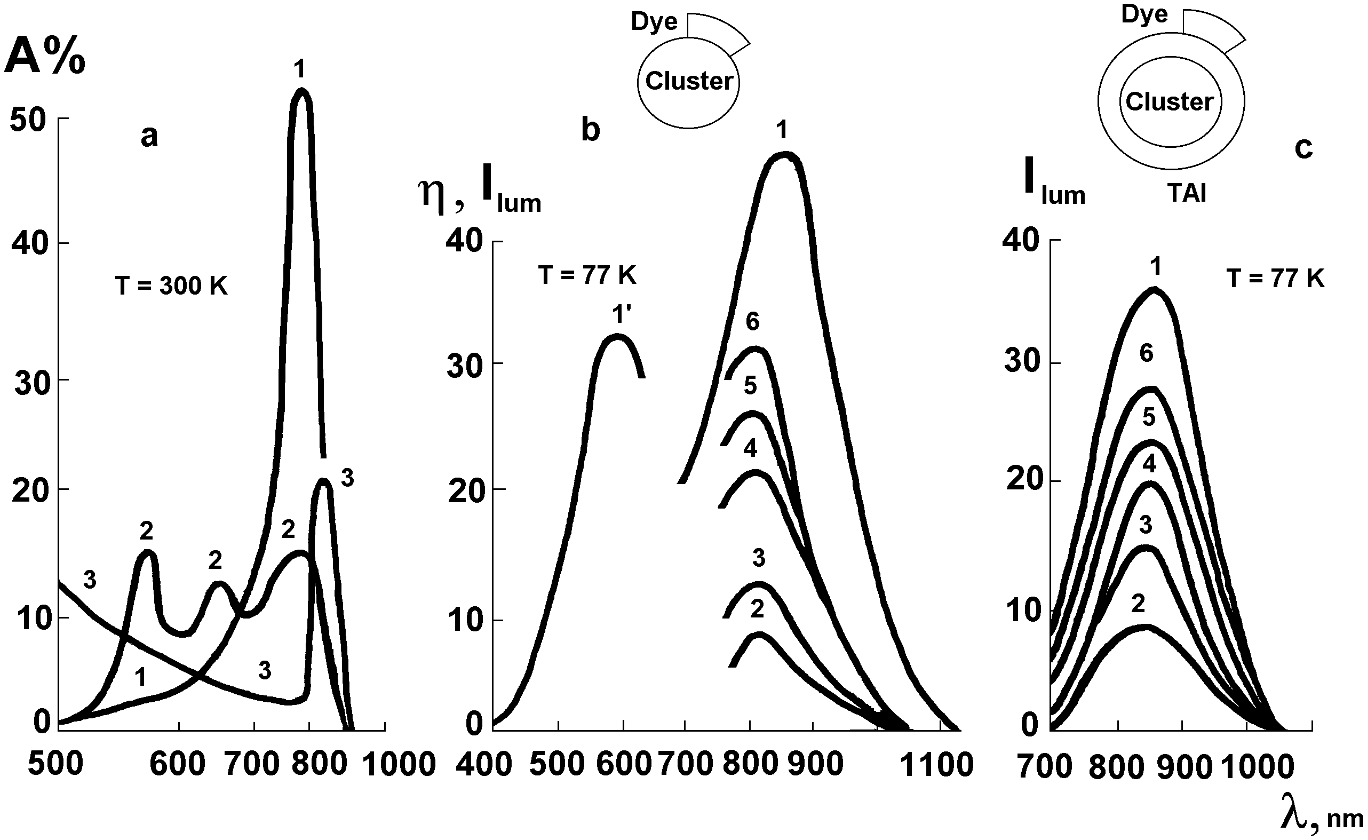

Figure 7. (a) Absorption spectra (T = 300 K): 1—Dye IV in 96% EtOH solution, Dye IV concentration is 10^{-4} M; 2—Dye IV in 5% solution of gelatin, Dye IV concentration is 10^{-4} M; 3—5% solution of gelatin containing silver sulfide clusters (5×10^{-3} M), TAI (0.02 gram/liter) and Dye IV (10^{-4} M). (b) Low-temperature (T = 77 K) luminescence spectra (1 through 6) and infrared luminescence excitation spectra (emission band with λ_{max} = 840 nm)(1′) of cooled 5% gelatin solution containing the silver sulfur clusters (1, 1′), and the silver sulfur clusters (5×10^{-3} M) and Dye IV (10^{-4} M) (2 through 6). Luminescence was excited by light with λ (nm): Curves 1 and 6 at 500; 2 at 420; 3 at 440; 4 at 460; 5 at 480 nm. (c) Low-temperature (T = 77 K) luminescence spectra for cooled 5% gelatin solution containing the silver sulfur clusters (5×10^{-3} M), TAI (0.02 g/L) and Dye IV (10^{-4} M) (Curves 2 through 6), Curve 1 shows luminescence spectra for cooled 5% gelatin solution containing only the silver sulfur clusters. Luminescence was excited by light with λ (nm): Curves 1 and 6 at 500; 2 at 420; 3 at 440; 4 at 460; 5 at 480 nm. Values I_{lum} and η are given in arbitrary units.

to the excited singlet level (S_1) of adsorbed dye. This conclusion can be substantiated under conditions where the silver sulfide clusters were formed by adding solutions of $AgNO_3$ and Na_2S in gelatin solution. After cluster formation, two types of samples were made: one by adding dye (sample K_1) and the other by adding TAI first and then dye (sample K_2). From the results shown in Fig. 6(b) (Curve 1′) in the case of sample K_1 with Dye I, luminescence excitation spectra of the silver sulfide clusters (emission band λ_{max} = 820 nm) have maxima at λ = 578 and 620 nm, resulting from absorption of light by the J-aggregate of dye and by the cluster itself, respectively. If the excitation wavelength λ = 500 nm (absorbed by the cluster) is used, then fluorescence spectra have M-(λ = 565 nm) and J-(λ = 600 nm) bands of dye (see, for example, Refs. 3, 5, and 21), as well as the emission band of the cluster [λ_{max} = 820 nm, Fig. 6(a), Curve 1]. The data point to the following possibilities:

- Excitation of cluster luminescence by absorption of light by J-aggregate of dye [the band λ_{max} = 578 nm, see Fig. 6(b), Curve 1′].
- Fluorescence excitation from both molecules and aggregates of dye adsorbed on clusters by the light absorbed mostly by the clusters [Fig. 6(a), Curve 1].

If the TAI layer is created between the cluster and dye (sample K_2), the light absorbed by the cluster does not excite fluorescence of adsorbed dye, and thus only luminescence of the cluster can be observed [Fig. 6(a), Curve 2]. On the other hand, the cluster luminescence can be excited in the M-band of adsorbed dye [Fig. 6(b), Curve 2']. These data also indicate that the presence of the TAI layer does not prohibit the relocalization of charge carriers from photoexcited, adsorbed dye onto the cluster [Fig. 6(b), Curve 2'] but does prevent the opposite process of relocalization of electron and hole from the excited cluster onto S_1 and ground (S_0) levels of dye, respectively. The properties of the system "cluster–TAI layer–dye" can be explained as follows.

Let us define τ_1 as the lifetime of the excited dye (in singlet or triplet states); τ_2 as the time necessary for an electron to tunnel through the TAI layer from the excited level of dye on one of the excited levels of the cluster or vice versa; and τ_3 as the relaxation time of the excited states of a cluster, i.e., the time necessary for an electron transfer from the upper excited states of a cluster on its lower excited states. If $\tau_1 > \tau_2 > \tau_3$, then the tunneling of an electron from the excited state of dye to the excited state of a cluster is possible, but the opposite tunneling process between these levels is impossible.

Results analogous to those mentioned above were also observed in the case of adsorption of IR dyes on the silver sulfide clusters. As an example, results are discussed in this article for 3,3’-diethyl-11-methyl-thiotri-

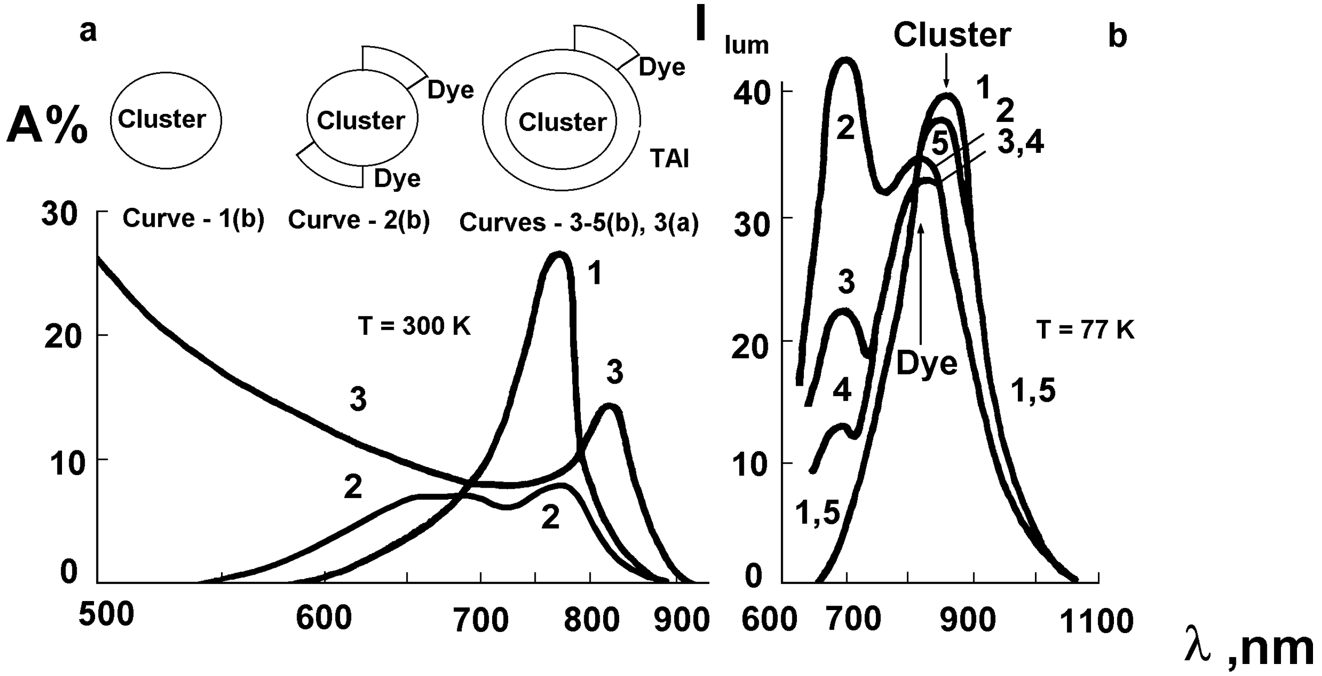

Figure 8. (a) Absorbtion spectra (T = 300 K): 1—Dye V (10^{-4} M) in 96% EtOH solution; 2—Dye V (10^{-4} M) in 5% gelatin solution; 3—5% solution of gelatin containing silver sulfur clusters (full concentration 5×10^3 M), TAI (0.02 g/L) and Dye V (10^{-4} M); (b) Low-temperature (T = 77 K) luminescence spectra for cooled 5% gelatin solution containing silver sulfur clusters (Curve 1) (5×10^{-3} M) and silver sulfur clusters, different concentration of TAI and Dye V (10^{-4} M) (Curves 2 through 5). The TAI concentrations (g/L): 2—0.0 (without TAI); 3—0.0002; 4—0.002; 5—0.02. Luminescence was excited by light with λ = 500 nm. Values I_{lum} and η is given in arbitrary units.

carbocyanine iodide (Dye IV, in photographic emulsion, has an absorption band with maximum at λ = 840 nm; $E_{1/2\,Red} = -0.85$ V, $E_{1/2\,Ox} = +0.24$ V) and for 3,3'-diethylthiotricarbocyanine iodide (Dye V, in ethanol solution (EtOH), has an absorption band with maximum at λ = 760 nm and in photographic emulsions, an absorption band with maximum at λ = 810 nm; $E_{1/2\,Red} = -0.78$ V, $E_{1/2\,Ox} = +\,0.28$ V). In Figs. 7(a) and 8(a), we show the absorption spectra (T = 300 K) of the following samples:

1. Dye in 96% EtOH solution; dye concentration 10^{-4} M—sample K_3 [Fig. 7(a), Curve 1 and Fig. 8(a), Curve 1].
2. Dye in 5% gelatin solution—sample K_4 [Fig. 7(a), Curve 2; Fig. 8(a), Curve 2; C = 10^{-4} M].
3. Silver sulfide clusters (5×10^{-3} M); TAI (0.02 g TAI/Liter) and dye (10^{-4} M) in 5% gelatin solution [sample K_2 type; Fig. 7(a), Curve 3 and Fig. 8(a), Curve 3).

In the absorption spectra of sample K_4 we observed an absorption band of the dye (λ_{max} = 790 and 780 nm for Dye IV and Dye V, respectively) and also short-wave bands [Figs. 7(a), Curve 2 and 8(a), Curve 2] possibly due to the decomposition products of dye molecules or to different products of bonding of water and alcohol molecules to dye (tentatively Dye′).[62]

In the absorption spectra of samples K_2 there is a long wavelength absorption band [Fig. 7(a), Curve 3 and Fig. 8(a), Curve 3] that confirms that formation of a layer of TAI on a cluster does not lead to desorption of dye into gelatin and that highly disperse particles of "silver sulfide cluster—TAI layer—adsorbed dye" type are formed in the solution of gelatin. In the samples K_1 excited with light (λ = 420 to 500 nm) that is not absorbed by dye but is absorbed by silver sulfide clusters, only the fluorescence of dye is observed [the emission band with λ_{max} = 820 nm for Dye IV, 680 nm (dye′), and 820 nm for Dye V; Figs. 7(b) and 8(b)]. If the TAI layer is formed between the cluster and the dye (sample K_2), the light absorbed by the cluster does not excite fluorescence of adsorbed dye and, thus, only luminescence of the cluster can be observed [Fig. 7(c), Curve 5 and Fig. 8(b), Curve 5]. These data suggest that the presence of the TAI layer prevents the process of relocalization of an electron and a hole from the excited cluster into the S_1—and ground levels of dye, respectively (Fig. 9).

In the case of infrared dyes, the relocalization of electron and hole from excited cluster to dye occurs very effectively in sample K_1. This is probably due to the appropriate position of the energy levels of dye relative to the energy levels of cluster and to the large size of dye molecules [Fig. 9(a)]. Thus, one can only observe the luminescence of adsorbed dye [Figs. 7(b), and 8(b)]. Because the efficiency of the charge carrier relocalization process in the case of samples K_2 depends on the thickness of the TAI layer, it has been observed that the luminescence intensity of adsorbed dye depends on the concentration of TAI in gelatin [Fig. 8(b), Curves 3 through 5]. Note that continuity of the TAI layer is an important condition for the relocalization process.

As can be seen from the scheme shown in Fig. 9(a), the values of the redox and oxidation potentials of clusters should be close to those of IR dyes ($E_{1/2Red} = -0.78$ V, $E_{1/2Ox} = +0.28$ V for Dye V). Further studies of dye sensitized cluster luminescence, using dyes with different redox and oxidation potentials, can improve data on the redox and oxidation potentials of the silver sulfide clusters.

These data are important for the better understanding of the supersensitizing action of TAI in sulfide sensitized emulsions.[63,64] According to the present results, the layer of TAI adsorbed on the silver sulfide cluster does not hinder the relocalization of charge carriers from

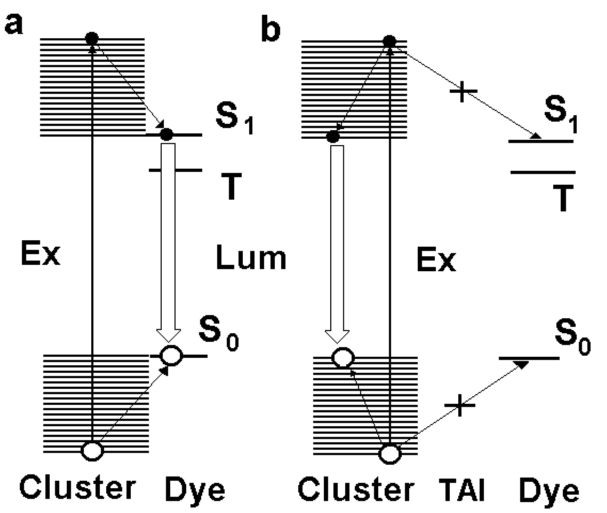

Figure 9. The schematic diagram of the energy levels in the systems "cluster–adsorbed dye" (a) and "cluster–TAI layer–adsorbed dye" (b). Electron transitions are shown as arrows, S_0 and S_1 are singlet dye levels, and T are triplet levels of dye.

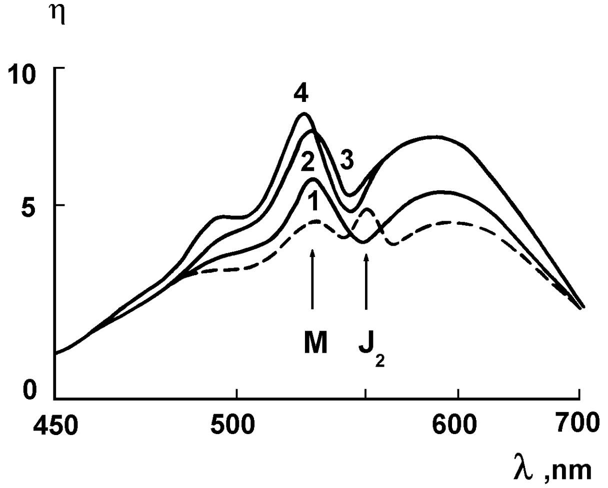

Figure 10. Infrared luminescence excitation spectra of sulfur sensitized AgBr emulsion containing 10^{-4} mol Dye III/mol AgBr and the following concentrations (mol/mol AgBr) of TAI: 1—0.0 (without TAI); 2—8×10^{-3}; 3—3×10^{-2}; 4—6×10^{-2}. The functions $\eta = f(\lambda)$ have been normalized on their values at $\lambda = 450$ nm. Value η is given in arbitrary units.

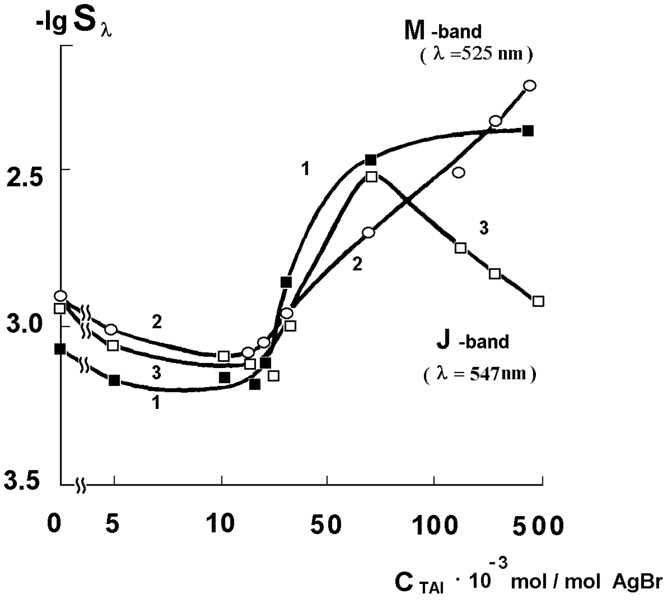

Figure 11. The dependence of the spectral sensitivity on TAI concentration in optimum sulfur sensitized AgBr emulsion (cubic, d = 0.15 m) with Dye III (3×10^{-4} mol dye/mol AgBr) in the following bands (λ_{max} , nm): 1—425 (intrinsic sensitivity); 2—525 (M - band); 3 - 547 (J - band).

excited dye to the cluster (transfer of electron from the excited Dye I to III to the cluster may also occur through silver halide), but reduces the possibility of back electron transfer from the excited states of the cluster to the lowest unoccupied energy level of adsorbed dye. Thus, a TAI layer inhibits the Type I desensitization processes.[65] The electron captured by the cluster can be used for silver deposit formation at the place of contact between the cluster and AgBr. In this case, the latent image centers $(Ag_2S_p)Ag_m^+$ are formed. It is also possible that, at room temperature, the TAI layer reduces the probability of the hole relocalization from excited or ionized dye into the cluster, and, therefore, weakens the Type II desensitization process, which is linked to the destruction of silver moieties in the latent image centers $(Ag_2S)_pAg_m^0$ (see Ref. 49) by holes. These results confirm the "insulation" mechanism of supersensitization suggested by Shapiro.[31,32]

Preferential adsorption of TAI on the mixed silver sulfide sensitivity centers $(Ag_2S)_pAg_k^+$ ($k < m = 4$)[41] lowers the probability of secondary dark reactions, which may increase the silver fragment size, and, as a consequence, transform the mixed cluster into a fog center. Antifogging as well as stabilizing action of TAI result from this effect.

The TAI layer, formed on the surface of silver sulfide clusters, not only diminishes the antiresonance effect in the system "cluster–adsorbed dye" but, in some cases, also has an influence on the adsorption of dye on the cluster [Fig.6(b), compare Curves 1' and 2'; the luminescence excitation spectra have a J-band in sample K_1 and an M-band in sample K_2]. We have observed this effect at relatively high concentrations of TAI in sulfur sensitized emulsions. As can be seen from Fig. 10, in the case of Dye III, dye adsorbs on the cluster with thick TAI layers as molecules, but not as J_2–aggregates. Furthermore, in complete agreement with the explanations given above, the formation of the TAI layer leads to a sharp increase of the efficiency (η) of the cluster's luminescence excitation under the irradiation with light in the spectral region where dye adsorbed on a cluster does not absorb. (For Dye III, it is a region of $\lambda > 560$ nm; compare Curves 1 through 4 in Fig. 10.) After the TAI layer reaches a certain thickness (h'), further increase of h' does not change η (Fig. 10, Curves 3 and 4, the region $\lambda > 560$ nm).

The supersensitization effect, connected to the adsorption of TAI on the silver sulfide or gold sulfide clusters, depends on the thickness of the TAI layer. Therefore, such an effect, in the first place, should be observed in sulfur or sulfur-plus-gold sensitized emulsions, and, in the second place, should depend on concentration of TAI, introduced into the emulsion. The results that we obtained support these conclusions. In fact, the supersensitization effect can be obtained only at TAI concentrations, $c > 10^{-2}$ mol TAI/mol AgBr (Fig. 11). The sensitivity decrease in the J-band (λ_{max} = 547 nm) and the sharp increase of sensitivity in the M-band (λ_{max} = 525 nm), can only be observed at relatively high TAI concentrations ($c > 5 \times 10^{-2}$ mol TAI/mol AgBr) (Fig. 11, Curves 2 and 3), correspond either to the above conclusions about influence of TAI on dye adsorption on the clusters, or to the break-up of J-aggregates by the TAI molecules (see, for example, Ref. 66).

Interaction of Adsorbed Dye with Emulsion Microcrystal Surfaces Modified by Chemical Sensitization

The results presented in this section are related to the case of direct adsorption of dye on the surface of AgBr MC. As the subject of our investigation, we have chosen AgBr emulsions containing cubic MC (d = 0.25 µm) sulfur sensitized (2×10^{-3} mol $Na_2S_2O_3$/mol AgBr, T = 47 C, pAg = 8.6—Emulsion A_1) or reduction sensitized (2.6×10^{-3} mol thiourea dioxide/mol AgBr, T = 43 C, pAg = 8.6—Emulsion A_2). Emulsions A_1 and A_2 with different duration of sensitization (ripening time, t_2) were deposited onto glass plates and then treated with 10^{-5} M solution of 1,1'-diethyl-2,2'-quinocarbocyanine chloride (Dye VI, $E_{1/2Red} = -1.10$ V, $E_{1/2Ox} = +0.58$ V)—Samples B_1 and B_2, respectively; or first washed in 1.7×10^{-3} M solution of N,N'-dimethyl-4,4'-bipyridylium dichloride (desensitizer VII, $E_{1/2Red} = -0.44$ V) and then treated with Dye VI (Samples C_1 and C_2, respectively).

As might be expected, we observed sharp decreases of both intrinsic (S) and spectral (S_λ) sensitivities in the absorption band (λ_{max} = 642 nm) of aggregated dye in the presence of typical desensitizer VII. Note the following:

- The t_2 dependence of intrinsic (λ = 400 nm) sensitivity for Emulsion A_1 and spectral (λ = 642 nm) sensitivity of Emulsion B_1 have the maxima at the same value of t_2 [analogous to Emulsions A_2 and B_2; Figs. 12(a) and 12(b); Curves 1 and 2]. Thus centers of sensitivity in Emulsions A_1 and B_1 are the same (analogous to Emulsions A_2 and B_2). At small t_2 values, a minimum for the function $S_\lambda = f(t_2)$ (λ = 642 nm) was observed for Emulsions C_1 and C_2 [Figs. 12(a) and 12(b), Curve 3].
- The minimum of the function $S_\lambda = f(t_2)$ (λ = 642 nm) for emulsion C_1 occurs at the same t_2 value as the maximum of the functions $\eta_{470} = f(t_2)$ and $\eta_{490} = f(t_2)$ for Emulsion A_1 [Fig. 12(a), Curves 4 and 5]. A similar result was observed also in the case of emulsions C_2 and A_2 [Fig. 12(b), Curves 4 and 5]. Here η_{470} and η_{490} are quantities proportional to the excitation efficiency of low-temperature (T = 77 K), orange luminescence for Emulsions A_1 and A_2 with excitation into bands[41] with λ_{max} = 470 and 490 nm.

To explain these data, let us recall the following:

- Increase of η_{470} and η_{490} during the initial stages of chemical sensitization (ripening) reflects the increase of the concentration of surface Br_s^- and I_s^- anions due to consumption of the surface and subsurface Ag^+ cations for impurity center formation.
- Desensitization of emulsions in the presence of Compound VII is caused by the trapping of a free electron by a molecule of desensitizer.
- The excited state (S_1) of Dye VI is located within the AgBr conduction band (CB) [$-E_{1/2Red}$ (dye) > $-E_{1/2Red}$ (AgBr)], but the lowest excited state of the J-aggregate can be found below the bottom of the AgBr CB, while the ground state (S_0) of J-aggregate is below the I_s^-–level and is above the top of the AgBr valence band (VB). In this case, the latent image for-

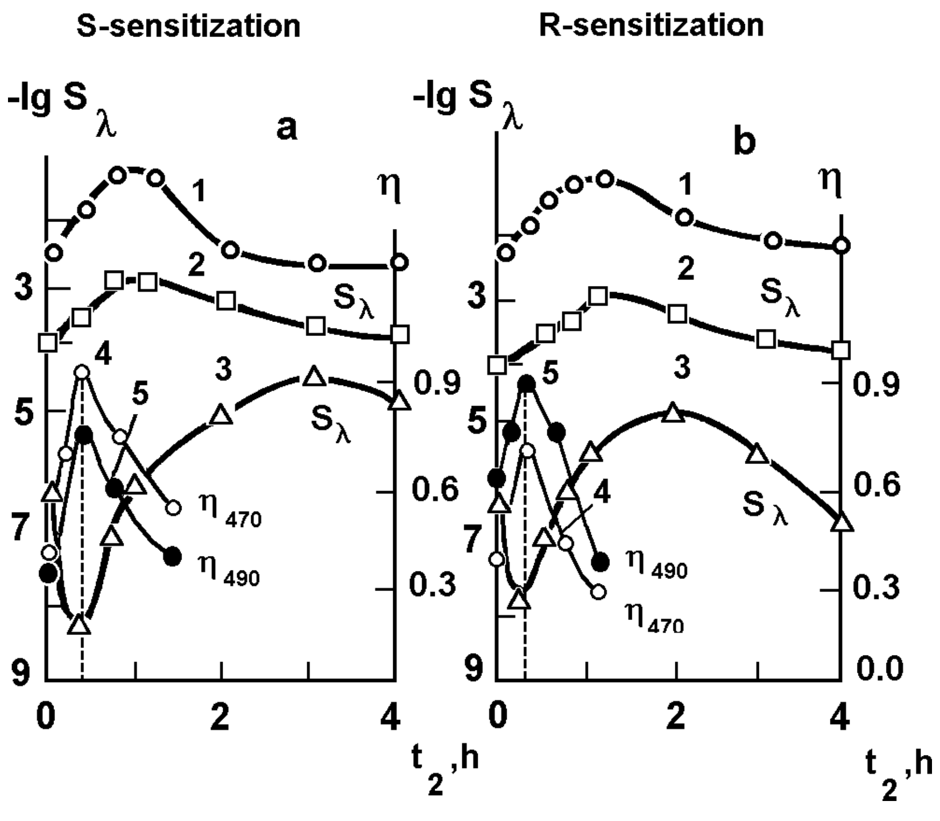

Figure 12. The dependence of the sensitivity for emulsion layers Type A_1 (1) and A_2 (1), B_1 (2) and B_2 (2), C_1 (3) and C_2 (3) at λ = 400 nm (Curve 1) and at λ =642 nm (Curves 2 and 3) on duration (t_2) of sulfur (a) and reduction (b) sensitization. Curves 4 and 5 are dependencies of values of η_{470} (4) and η_{490} (5) on t_2 for emulsion layers A_1 (a) and A_2 (b). Values η_{470} and η_{490} are given in arbitrary units.

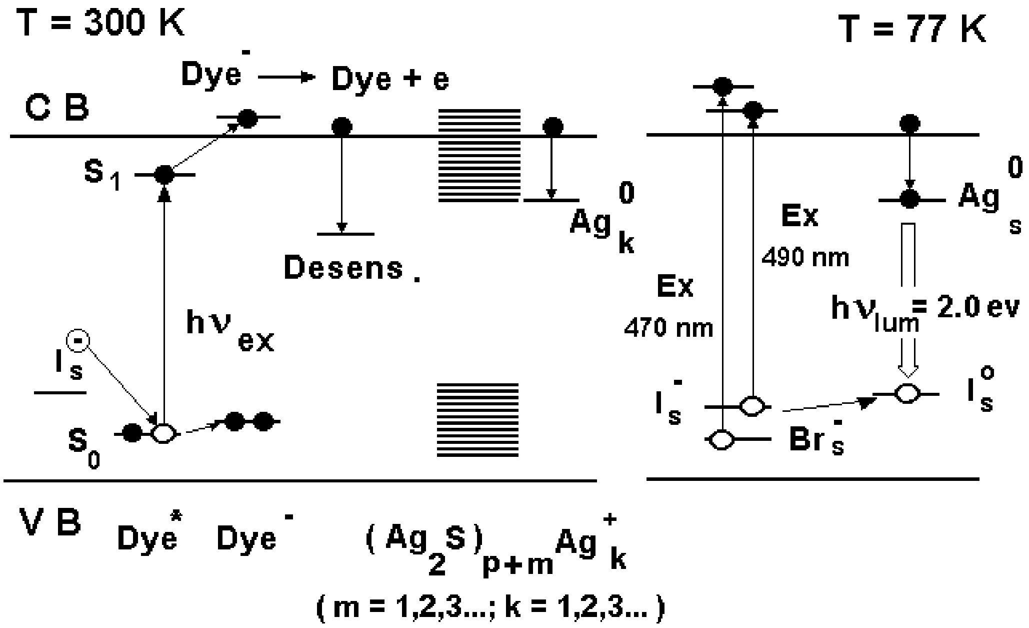

Figure 13. The schematic energy level diagram of AgBr with adsorbed dye, silver sulfide clusters, and the desensitizer (Desens.). The role of I_s^--anions in the mechanisms of supersensitization (T = 300 K) and luminescence (T = 77 K) is shown.

mation, after light absorption by J-aggregate, can be described by:

$$\text{Dye} + h\nu \Rightarrow \text{Dye}^* (S_1),\ \text{Dye}^* \Rightarrow^{kT} \text{Dye}^+ + e$$
$$\text{(in AgBr CB)}$$
$$(Ag_2S)_pAg_k^+ + e \Rightarrow (Ag_2S)_pAg_k^0 +$$
$$Ag_{s,i}^+ \Rightarrow (Ag_2S)_pAg_{k+1}^+ \Rightarrow \ldots, \qquad (6)$$

$$\text{Dye}^+ + I_s^- \Rightarrow \text{Dye} + I_s^0,$$

$$\text{Dye}^* (S_1) + (Ag_2S)_pAg_k^+ \Rightarrow (Ag_2S)_pAg_k^0 + Ag_{s,i}^+ + \text{Dye}^+$$
$$\Rightarrow (Ag_2S)_pAg_{k+1}^+ + \text{Dye}^+$$

$$\text{Dye}^+ + I_s^- \Rightarrow \text{Dye} + I_s^0, \qquad (7)$$

$$\text{Dye}^* (S_1) + I_s^- \Rightarrow \text{Dye}^- + I_s^0,\ \text{Dye}^- \Rightarrow \text{Dye} + e$$
$$\text{(in AgBr CB)}$$

$$(Ag_2S)_pAg_k^+ + e \Rightarrow (Ag_2S)_pAg_k^0 +$$
$$Ag_{s,i}^+ \Rightarrow (Ag_2S)_pAg_{k+1}^+ \Rightarrow \ldots, \qquad (8)$$

where I_s^- are the surface anions that may or may not belong to the donor–acceptor pairs ($Ag_s^+ \ldots I_s^- Br_s^-$) and $Ag_{s,i}^+$ is a mobile surface or interstitial silver ion. Reaction 7 represents the latent image center formation on direct transitions of the electron from the excited state of dye to the sensitivity center.

All obtained data clearly indicate that in the mechanism of spectral sensitization a significant role belongs to the surface I_s^- anions which act like supersensitizers, reducing excited dye[25,55] (Reaction 8). With the increase of the concentration of the surface anions, the importance of Reaction 8 increases sharply compared to that of Reaction 7. The electron that appears in the conduction band according to Reaction 8 can be captured by the sensitivity center (immediately or after a series of relocalizations on shallow traps) or by the desensitizer (Fig. 13). The data shown in Fig. 12 (Curve 3) indicates that the electron capture cross section (σ_e) of impurity centers emerging at the initial stage of chemical sensitization is less than σ_e of the desensitizer. The increase of the sensitivity of C_1 and C_2 emulsions at the later stages of ripening (after S_λ passes through the minimum) confirms that during chemical sensitization, one can observe the increase of both the energy depth of electron traps[41,53,67] and the electron capture cross section of the sensitivity centers (see also Ref. 68). The latter is likely to be connected to the increase of the geometric size of the sensitivity centers $(Ag_2S)_{p+m}Ag_k^+$ (m = 1,2,3...; k =1,2,3) in sulfur or Ag_n^+ (n = 1,2,3) in reduction sensitization.

The evolution of centers at sulfur sensitization occurs according to the scheme

$$Ag_2S \Rightarrow (Ag_2S)_2 \Rightarrow (Ag_2S)_3 \Rightarrow \ldots \Rightarrow (Ag_2S)_n \text{ (hole trap)}$$
$$\Rightarrow \ldots \Rightarrow (Ag_2S)_p \Rightarrow (Ag_2S)_pAg_k^+ \text{ (an electron trap)}$$
$$\Rightarrow (Ag_2S)_{p+m}Ag_k^+ \ (p > n;\ m=1,2,3\ldots;\ k = 1,2,3),$$

where clusters $(Ag_2S)_pAg_k^+$ or $(Ag_2S)_{p+m}Ag_k^+$ (m = 1,2,3...; k=1,2,3) are identified with the sensitivity centers.[40,41]

The increase of the electron capture cross section of the sensitivity centers is also the cause of the decrease of η_{470} and η_{490} in the A_1 and A_2 emulsions (Fig. 12, Curves 4 and 5).

If the highest occupied electron level of dye⁻ is below the bottom of AgBr CB, then Reaction 8 is extremely important for spectral sensitization for the following reasons (often discussed in the literature):

- The lifetime of dye⁻ anion-radical is significantly longer than the lifetime of excited dye* (so-called kinetic aspect of the spectral sensitization process[69]).
- The depth of the energy level of dye⁻ relative to the bottom of the AgBr CB is less than that of dye* (so-called energetic aspect of the spectral sensitization process);
- The depth of energy level I_s^0 relative to the top of AgBr VB is larger than that of dye⁺. Thus, the probability of latent image center destruction by holes that can be thermally liberated into the valence band from local levels decreases.

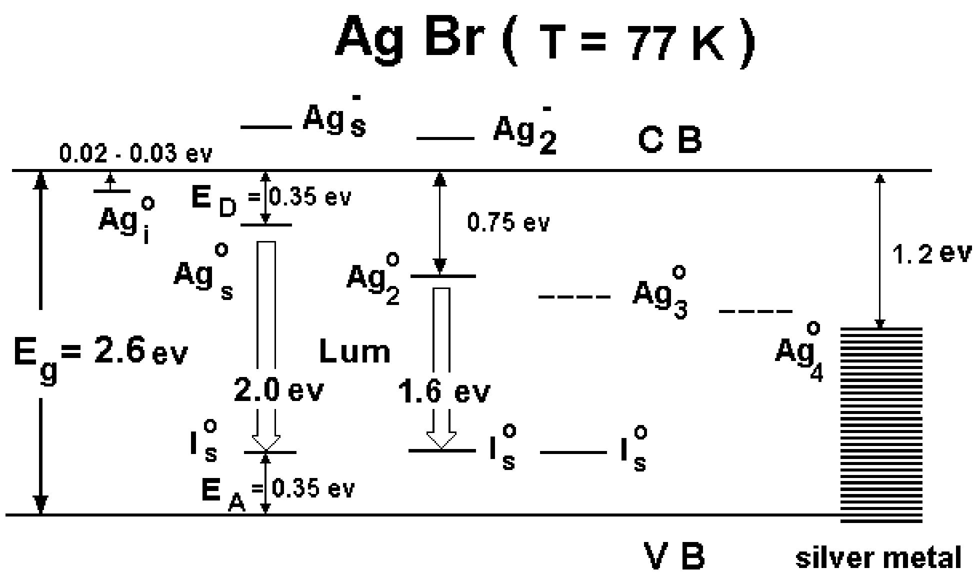

Figure 14. The schematic energy level diagram of AgBr at T = 77 K with electron–hole transitions that determine DAP luminescence. The positions of the Ag_3^0 and Ag_4^0 energy levels are presumed because of the lack of experimental data, and E_D and E_A are the donor (Ag_s^0) and acceptor (I_s^0) binding energies, respectively.

If the I_s^- anion belongs to the donor–acceptor pair, then (Ag_s^+ ...$I_s^0Br_s^-$) and dye$^-$ emerges as a result of supersensitization, then subsequently, in the emulsions without chemical sensitization, the following processes can be observed:

$$\text{Dye}^- \Rightarrow \text{Dye} + e, \quad (Ag_s^+ ... I_s^0 Br_s^-) + e \Rightarrow (Ag_s^0 ... I_s^0 Br_s^-) + Ag_{s,i}^+ \Rightarrow (Ag_2^+ ... I_s^0 Br_s^-) \quad (9)$$

As shown earlier,[41,67] transformation of Ag_s^0 into Ag_2^+ at room temperature is faster than interaction of the hole (I_s^0) with Ag_s^0. Therefore, even in the chemically unsensitized emulsions, I_s^- anions can also cause increase of effectiveness of the spectral sensitization [in the case of dyes with oxidation potential $E_{1/2Ox}$ (dye) > $E_{1/2Ox}$ (I_s^-)].

If the ground state (S_0) of dye is higher than the I_s^- level relative to the top of the AgBr valence band and the excited level S_1 is below the AgBr conduction band, then, as we known, spectral sensitization can occur either as a result of thermal ionization of S_1 or by the electron transition from S_1 directly to the impurity centers or levels of surface silver ions.[70] This latter phenomenon is especially relevant for infrared dyes.

Determination of Thresholds for Electron and Hole Transfer Processes in Spectral Sensitization on the Basis of Luminescence

Results given in the previous section confirm a significant role for surface anions of MC in the mechanism of spectral sensitization of photographic emulsions. Therefore, additional attention should be given to the following. It is known that orange luminescence of AgBr MC is[41] due to I_s^- surface anions. This luminescence is a result of radiative recombination in donor–acceptor pairs (DAP)[41,53] (see schemes 3, 4, and Fig. 14). The emission energy of DAP is given by

$$h\nu = E_g - (E_D + E_A) + e^2/\varepsilon r, \quad (10)$$

where E_g is the band gap energy; E_D and E_A are the donor and acceptor binding energies, respectively, e is the static dielectric constant, and r is the pair separation distance.

To determine E_D and E_A, we can use the results of the low-temperature photoconductivity measurements on AgBr emulsion MC[71,72] as well as the results of the excitation-induced absorption spectroscopy of AgBr at low temperatures.[73] It was shown[71] that in AgBr MC unexposed to radiation there exist two types of electron trapping centers, with thermal activation energies ΔE_1 = 0.02 eV and ΔE_2 = 0.20 eV (according to Ref. 72 ΔE_2 = 0.28 eV). It is known that for atomic centers in solids the thermal activation energy is ca. 2/3 of the optical activation energy.[74] But the study of excitation-induced absorption spectra of AgBr under UV irradiation, at various temperatures, has shown[73] that electron capture centers determine absorption bands at 0.02, 0.3 and 0.75 eV. Note that the energy level of the surface Ag_2^0 center lies[41,53,67] 0.4 eV deeper into the band gap than the energy level of Ag_s^0. Thus, it can be assumed that these energies 0.02 to 0.03, 0.3 to 0.4, and 0.75 eV determine the position of the energy levels of the following centers (relative to the bottom of AgBr conduction band): interstitial Ag_i^0 atom (see also Refs. 75 and 76), surface Ag_s^0 atom, and Ag_2^0 center, respectively (Fig. 14). Therefore, in Eq. 10 one can assume E_D = 0.3 to 0.4 eV. (For further calculations we will use the average value of E_D = 0.35 eV.)

The studies of AgBr or AgBr(I) luminescence (T = 77 K) help to establish that in AgBr there exists hole trapping levels with a depth of 0.3 to 0.4 eV relative to the top of the valence band of AgBr.[73] This level can be assigned to the adventitious impurity surface I_s^- anions because they, as shown in Ref. 41, create hole trapping levels from 0.24 to 0.56 eV above the top of the AgBr valence band. Based on these results it is also possible to accept E_A = 0.3 to 0.4 eV in Eq. 10. (As before, we will use the average value of 0.35 eV, see Fig. 14.)

With the increase of temperature, E_g of AgBr decreases. Taking into account that $dE_g/dT = -1.3 \times 10^{-3}$ eV/K (see, for example, Ref. 77), we can draw the conclusion that when temperature increases from 77 to 300 K the value of E_g decreases by 0.29 eV. Therefore, at room temperature E_D = 0.20 to 0.25 eV and E_A = 0.20 to 0.25 eV. Values found for E_D and E_A coincide with the depths of thresholds for desensitization and internal fog bleaching by photoexcited dye[78–81] that have been determined in studies of the spectral sensitization. Such coincidence, once more, stresses the significant role of both the surface silver cations and the surface Br_s^- and I_s^-

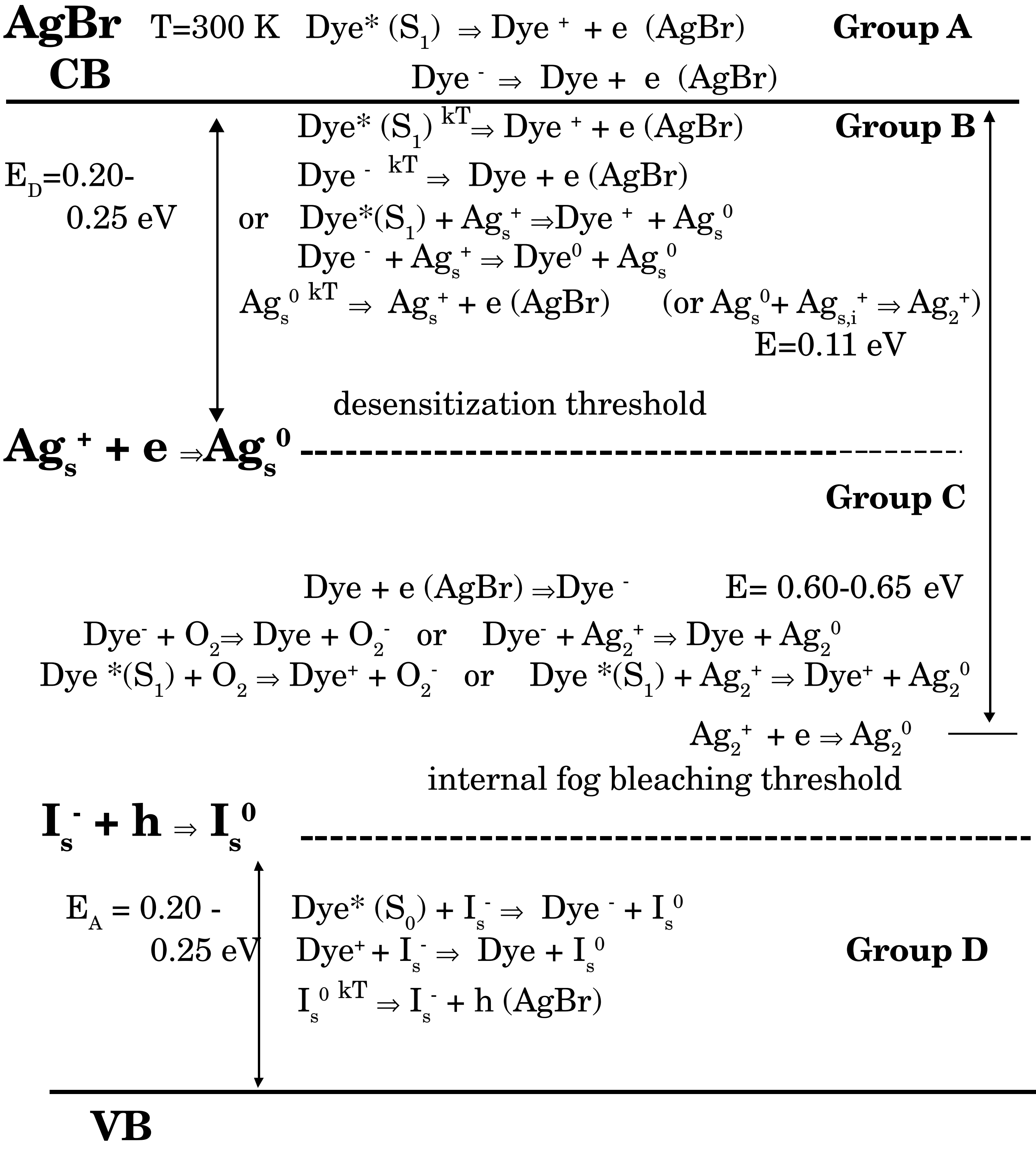

Figure 15. The schematic energy level diagram of AgBr at T = 300 K with reactions representing the participation of dyes with different reduction–oxidation potentials in the mechanism of spectral sensitization. The values E_D and E_A are the donor (Ag_s^0) and acceptor (I_s^0) binding energies, respectively.

anions of emulsion MC in the mechanism of spectral sensitization (see also Refs. 69 and 82).

Electron capture by Ag_s^+ stimulates the formation of Ag_2^+ and Ag_3^+ centers, which are deep electron traps:

$$Ag_s^+ + e\ (\text{from AgBr CB}) \Rightarrow Ag_s^0\ ; \quad Ag_s^0 + Ag_{s,i}^+ \Rightarrow Ag_2^+, \tag{11}$$

$$Ag_2^+ + e\ (\text{from AgBr CB}) \Rightarrow Ag_2^0; \quad Ag_2^0 + Ag_{s,i} \Rightarrow Ag_3^+ + e\ (\text{from AgBr CB}) \Rightarrow Ag_3^0\ , \tag{12}$$

where $Ag_{s,i}^+$ is a mobile interstitial or surface silver ion. The activation energy corresponding to Eqs. 11 and 12 is[83] E = 0.11 eV, which coincides with the mobility activation energy of the interstitial or surface silver ions.

It is well known that O_2 molecules are always present on the surface of emulsion MC. These molecules can capture an electron from the AgBr conduction band, and, thus, they impede Reactions 11 and 12. The desorption of O_2 molecules, during air evacuation, increases efficiency of latent image center formation.[84,85] The results presented above allow us to establish some details of the spectral sensitization mechanism by using dyes with different redox potentials. According to their role in the spectral sensitization process, dyes can be tentatively divided into four groups (Fig. 15, see also Refs. 18, 86, and 87).

Group A. The excited level S_1 of dye or the highest occupied electronic level of anion-radical dye$^-$ (anion-radical dye$^-$ appears as a result of reduction of excited dye*) are in the conduction band of AgBr. The electron appearing in the conduction band of AgBr can be captured by the surface silver cation Ag_s^+ or by a sensitivity center. Such dyes are effective spectral sensitizers.

Group B. The excited level S_1 of dye or the highest occupied electronic level in anion-radical dye$^-$ are located between the bottom of the AgBr conduction band and the electron capture level of the surface Ag_s^+ ion. After absorption of light by such dyes, appearance of the electron in the AgBr conduction band is possible as a result of a thermally activated process. In addition, the electron can tunnel from excited dye* or dye$^-$ to the surface Ag_s^+ ion. The appearance of Ag_s^0 promotes latent image center formation according to Reactions 11 and 12. Note that an electron can appear in the conduction band according to the reaction $Ag_s^0 \Rightarrow Ag_s^+ + e$, which is a thermally activated process.

Group C. The excited level S_1 of dye and the highest occupied electronic level of anion-radical dye$^-$ are located below the electron capture level formed by the surface Ag_s^+ ion. Such dyes can capture an electron from the conduction band of AgBr and impede Reactions 11 and 12. Thus, these dyes decrease the effectiveness of latent image center formation, and therefore act as desensitizers.

Group D. The ground state of these dyes (S_0) is above the top of AgBr VB, but is not higher than the hole localization level of the surface I_s^- anion. When such a dye absorbs light, Reactions 1 and 2 are feasible with formation of I_s^0 or $I_s^0I_s^-$ in the case of AgBr(I). Furthermore, thermal activation of a hole into the AgBr VB ($I_s^0 \Rightarrow I_s^- + h$) and the participation of this hole in the destruction of internal fog centers[78] are possible. It is clear that for dyes from Group D, light-induced ESR signals of dye$^+$ can not be observed (see, for example, Ref. 88).

The classification of dyes into groups A, B, C, and D, with respect to the spectral sensitization mechanism, agrees with the kinetic model of spectral sensitization.[69]

The appearance of Ag_s^0 on irradiation of emulsion MC leads in turn to formation of deep surface electron capture centers Ag_2^+ and Ag_3^+ (see Reactions 11 and 12). In the absence of adsorbed desensitizers (particularly oxygen) the efficiency of electron capturing by these centers sharply increases. The direct electron transition from excited dye or from anion-radical dye$^-$ to the levels of surface Ag_2^+ centers allows spectral sensitization of photographic emulsions by dyes that have a sufficiently low value of reduction potential.[86,89] The appearance of Ag_2^+ can then occur according to the following reaction:

$$\mathrm{Dye}^- + Ag_{s,i}{}^+ \Rightarrow \mathrm{Dye}\ Ag_s^0 \Rightarrow Ag_s^0 + Ag_{s,i} + \Rightarrow Ag_2^+ \quad (13)$$

According to the proposed models, the process of fog bleaching by photoexcited dye is determined by the hole relocalization from dye* to the surface I_s^- anions, which are the hole capture centers. Iodide anions are adventitious impurities in AgBr. Their concentration in AgBr emulsion MC and vacuum evaporated AgBr layers can differ to a large extent. Therefore, data obtained by studying the process of fog bleaching by photoexcited dye in photographic emulsions compared to vacuum evaporated AgBr layers can be different.[90]

As is well-known, decrease of the pAg value of a photographic emulsion leads to appearance on the surface of the emulsion MC, silver centers which are electron traps.[91,92] According to the scheme shown in Fig. 15, on creation of silver centers, e.g., Ag_2^+, there occurs a possibility of spectral sensitization by dyes with low reduction potential, as a result of direct transfer of electrons from the excited S_1 level of the dye into the lowest unoccupied level of the Ag_2^+ (or Ag_3^+) center, that have appeared owing to the reductive function of the gelatin. Therefore decrease in the pAg value of emulsion is followed by an increase in the effectiveness of spectral sensitization by infrared dyes,[93,94] that are characterized by a low reduction potential.

The significant role of the surface silver cations of emulsion MC, as acknowledged in numerous publications, allowed introduction of the concept of a sub-conduction electronic band due to these cations.[70] Similarly, the results presented in this paper prove an important role of MC surface anions in the process of spectral sensitization. Therefore, analogous to the conclusions made in Ref. 70, we can propose a concept of a hole band due to MC surface anions. Thus, using results of luminescence studies of spectrally sensitized photographic emulsions, we can give an explanation for the appearance of the thresholds for the processes of desensitization and bleaching of internal fog from the point of view of basic physics.

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