

Spectral Sensitization of AgHal Emulsions in the Near IR Region of the Spectrum with Thiocarboyanine Dyes

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Abstract

The spectral sensitization of AgBrJ emulsion is studied by new thiocarboyanines with dimethylene group in the chain. It is shown that such dyes form J-aggregates in the far red and near IR regions of the spectrum having high photochemical activity. Methods are developed of the new dyes J-aggregates supersensitization. It is found that spectral sensitization efficiency in the near IR region is close to that achieved in the red region of the spectrum.

Introduction

It is known that the thiocarboyanines (TCC) are traditionally used for spectral sensitization of AgHal emulsions in orange-red region of the spectrum. The most effective spectral sensitizers form J-aggregates, which absorption bands are bathochromic shifted relative to the molecular bands on 80-100 nm. An introduction of C_2H_5 -group in a mezo-position of the polymethine chain as well as replacement in heterocyclic nuclea promote the J-aggregation. Today practically for the all black-and-white and color photographic materials high efficient J-aggregates of TCC are used. The region of the spectral sensitization with J-aggregates of TCC is extended down to 700 nm.

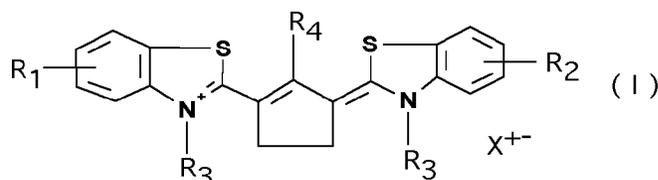
For the spectral sensitization in more long-waved spectrum region with $\lambda > 720$ nm, as a rule, thiadicarboyanines (TDCC) are used. Unlike the TCC, thiadicarboyanines are less inclined to J-aggregation and are applied in the molecular form. For this reason as well as because of desensitizing properties of TDCC, level of the spectral sensitivity in the region with $\lambda > 720$ nm is significantly less than in the red region of the spectrum.

It was shown earlier,¹ that introduction of dimethylene group in the external polymethine chain of TCC causes significant bathochromic shift of the absorption. According to the quantum-chemical calculations² it is connected with electronic influence of the methylene groups in 8,10-positions of the molecule. Introduction of dimethylene bridge increases the energy of the high-occupied molecular orbital (ϵ_{h_0}) and thereby cause the bathochromic shift of the absorption maximum.

In this connection such dyes are of interest for expansion of the spectral sensitization zone by the thiocarboyanines to the far red and near IR region of the spectrum.

Experimental

In the present work TCC of the following structures are investigated:



where $R_1=R_2 = 4,5$ -benzo; $R_1=R_2=5$ -Cl; $R_1=R_2=5$ -OCH₃; $R_3=C_2H_5$, (CH₂)₃, SO₃; $R_4 = H, CH_3$ and $X^+ =$ counterion.

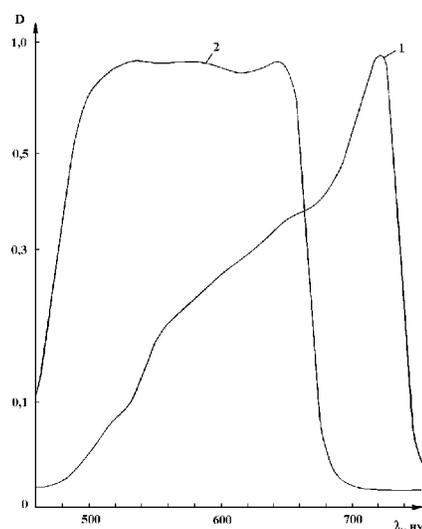


Figure 1. Absorption spectra for cubic crystal sensitized by Dye-1(1) and Dye-2(2).

Spectral sensitization was studied on AgBr(J) emulsions of the various form: cubic (100), $l = 0,22\mu$; octahedral (111), $d = 0,28\mu$ and T-crystals, $l = 1,0\mu$, $l/h = 10$. The emulsions were with S + Au sensitization.

It was shown that on cubic and T-crystals the dyes with the structure (I) form long-waved J-aggregates with $\lambda_{\max} > 700\text{nm}$. The most long-waved J-aggregates ($\lambda_{\max} = 720\text{nm}$) were observed for 3,3'-diethyl-5,5'-dimethoxy-8,10-dimethylenethiacarbocyanine tosylate (Dye-1, Fig.1, curve 1). For comparison on the Fig.1 the absorption of the J-aggregate of 5,5'-dimethoxy-substituted thiocarbocyanine with 9-C₂H₅-group (Dye-2, curve 2) is given.

The formation of the long-waved J-aggregates on octahedral AgHal microcrystals is hindered. It is characteristic that dyes with a structure (I) on cubic and T-crystals with S + Au-sensitization bring about the fogging ($D_o > 2,0$). Because a fog was absent on emulsions without S + Au-sensitization and increase during chemical sensitization, a conclusion was made that the contact fog is generated from interaction of J-aggregates of the dye with impurity (Ag,Au)S-centers. Reduction property of the dyes can be connected with the acidity of the methylene groups and with their ability in anionic state to oxidize on the impurity center to ethylene bond with removal of two electrons and two protons. Hence, such dyes can be used for chemical fogging of the photographic emulsions.

It is shown that the fog significantly decreases on introduction to the emulsion before dyes of the substances, which selectively adsorb on (Ag,Au)S-centers and thereby isolate the J-aggregates from impurity centers.³ To such compounds, some cyanine dyes, for example, thiamonomethinecyanines are concerned. The significant reduction of the fog was observed also on introduction to emulsion of an acid, depressing the acid dissociation of the dimethylene bridge.

It is established that J-aggregation of the dyes with the structure (I) on octahedral AgHal microcrystals is promoted by modification of the microcrystals surface by thiocyanate ions. It is illustrated on the Fig. 2.

It is shown, that the J-aggregates of the new dyes undergo to significant supersensitization both on the mechanism of dye hole trapping,⁴ and on the "isolation" mechanism.⁵ It is established, that efficiency of the spectral sensitization in the near IR region of the spectrum is close to the achievable in the red zone of the spectrum.

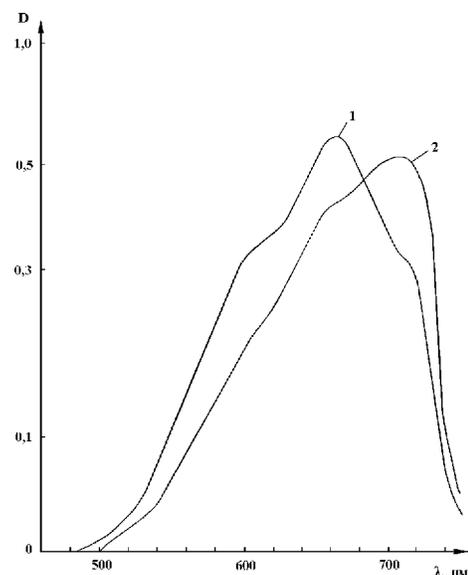


Figure 2. Absorption spectra for octahedral crystal sensitized by Dye-1 without (1) and with KCNS (2).

Conclusion

In result of the performed work it is possible to make the conclusion, that with the help of the J-aggregates of the thiocarbocyanines it is possible the effective spectral sensitization in the far red and near IR regions of the spectrum.

References

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