

Interaction Dye-Dye on a Surface of AgHal T-grains

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Abstract

In the present work the interaction between a series of not aggregating and J-aggregating monomethincyanins and series of J-aggregating thiacarbocyanine dyes (TCC) with the various substituents in 5,5 '-positions of heterocycles is investigated.

The object of investigation was a photographic emulsion containing a AgBrI T-grains of structure core - shell (d=1 μm, aspect ratio 1:10) with (S+Au)-sensitization.

As a result of the carried out investigation confirmed, that under activity of monomethincyanins occurs hypsochromic shift of J-bands TCC, accompanying by increase of desensitization. In case for not aggregating monomethincyanins the increase of intensity of absorption and bathochromic shift of their M - bands is marked. In case of J-aggregating monomethincyanins the decrease of intensity of absorption and hipsochromic shift of their J-bands is marked. The apparent effects depend on a charge of molecules of interreacting dyes and from a structure of the substituents in heterocycles of the investigated dyes. The effects are as much as possible expressed in case of an identical structure of heterocycles and substituents. The quantity of shift of J-bands TCC achieves in some cases 30 nm. The chemical (S+Au) - sensitization does not render influence on interaction between dyes. The summary, about an possibility of formation on a surface of AgHal T-grains of mixed J-aggregates consisting of molecules of monomethincyanins and TCC is made.

Introduction

In work [1] as supersensitizers of monodispersible photographic emulsions with (S+Au) - chemical sensitization the elementary thiamonomethincyanine dyes are offered. Their activity is accord by conformity of distance between atoms of silver and sulfur in $(Ag_2S)_n$-centre of sensitivity to distance between atom of nitrogen of a benzthiazole nucleus and methine atom of carbon of an outside polymethine chain of thiamonomethincyanine. It results in selective adsorption of thiamonomethincyanine on these centres and to their isolation from J-aggregate of carbocyanine dye. But at study of supersensibilizirending ability of thiamonomethincyanine on an emulsion without chemical sensitization was shown [2], that between J-aggregate TCC and elementary thiamonomethincyanins the interaction such as “dye – dye” is possible. This interaction results in change of spectral properties of J-aggregate TCC and increase it desensitisating activity. The purpose of the given work is study of interaction “dye – dye” on a surface T-grains AgHal with (S+Au) - chemical sensitization. It is necessary to determine what influence on the given interaction renders a structure of heterocycles of dyes. For this purpose, besides thiamonomethincyanine, other dyes were investigated also.

Experiment

All experiments are carried out on AgBrI photographic emulsion with T-grains such as core – shell (core AgBr, shell AgBrI, d = 1.0 μm, aspect ratio 1:10), with optimal (S+Au) - chemical sensitization. The structural formulas of some cyanine dyes are shown in a fig. 1. All dyes were added into an emulsion in amount 0.3 mmole/mole AgBrI separately and simultaneously. In the last case solutions of individual dyes mixed directly before addition in an emulsion. The photographic characteristices of emulsion determined reference sensitometric method. Blue sensitivity was determined behind an blue light filter (λ < 450 nm), spectral sensitivity was determined behind an red light filter (λ > 640 nm). A degree of desensitization (DD) was determined as the relation of blue sensitivity of an emulsion without dye to blue sensitivity of an emulsion with dye. The absorption spectrums of dyes in a emulsion was measured on a spectrophotometer SF-18.

For determination of a relative arrangement of highest filled electronic levels HOMO of various J-aggregates TCC carried out experiments on bleaching by holes TCC previously of created latent photographic image. For this purpose an emulsion fogged by light up to a level of optical density of a fog D_0 2,5. Bleaching of emulsion carried out at the presence of electron acceptor methylviologen [3].

Results and discussion

In tab. 2 some spectral and photographic characteristices of emulsion on a basis AgBrI T-grains, sensitized TCC and their compositions with III-X are given.

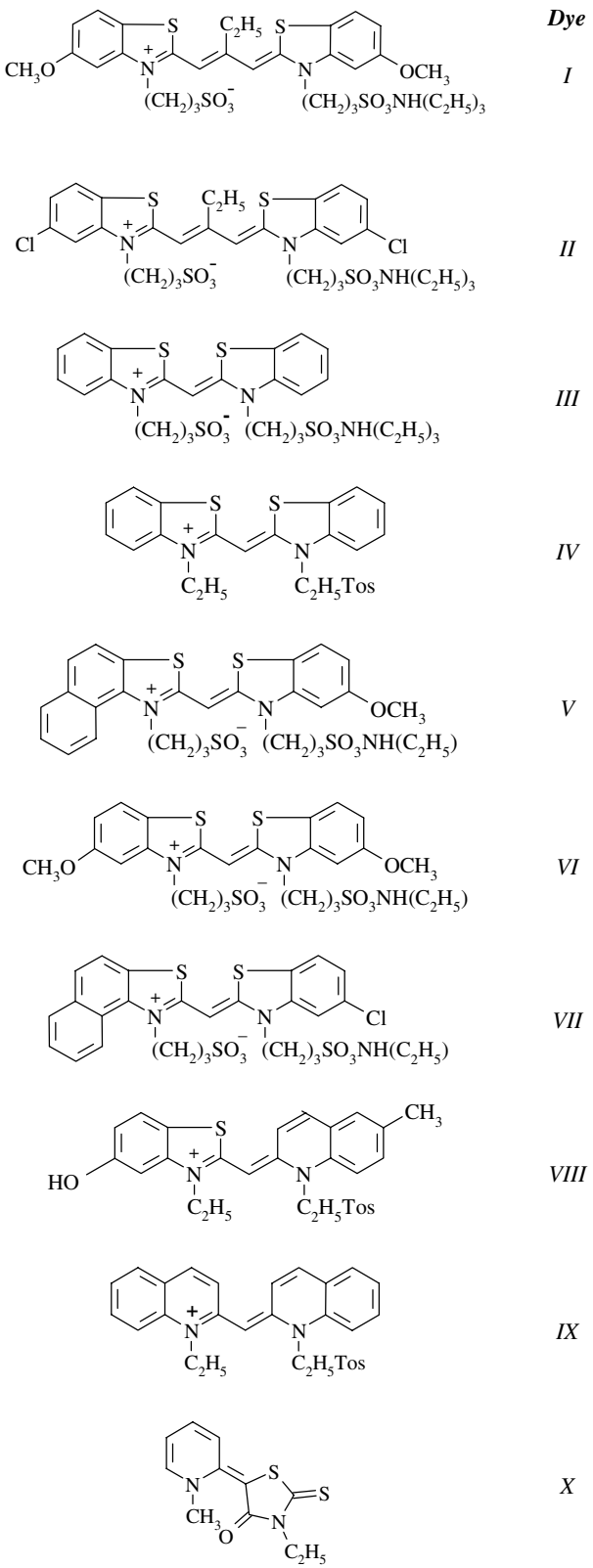

Figure 1. Structural formulas of cyanine dyes

Both TCC individually and at the presence of dyes III-X form J-aggregates on a surface AgBrI T-grains. However at presence III-IX the hypsochromic shift of J-band TCC is observed, which quantity depends on a structure TCC, on a structure of dyes III-IX and from the order of addition of dyes in an emulsion. In one cases the complete degradation of an initial J-band TCC and formation of new J-band TCC takes place(see fig. 2). In other cases the formation of a new J-band TCC occurs with some degradation of an initial J-band TCC. The emulsion have photographic sensitivity in an absorption zone of hypsochromic J-aggregates TCC.
Hence, desorption TCC from a surface AgBrI T-grains in a gelatine phase of an emulsion under influence IV - IX here does not take place.

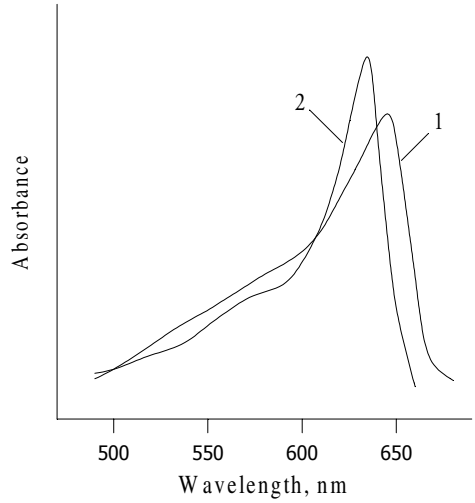

Figure 2. Absorption spectra of emulsion, containing dye I (1) and composition of dyes I and IV (2)

The spectral characteristic of absorption bands III-IX change at a combination of the given dyes with TCC. In case of elementary thiamonomethincyanine III and IV, which are on a surface AgBrI T-grains in a molecular state, take place a increase of intensity of absorption and batochromic shift on 2-9 nm of their M - bands. In case of J-aggregating on a surface AgBrI T-grains of monomethincyanins V-IX take place a decrease of intensity of absorption of their J-bands accompanying by their hypsochromic shift. The quantity of this shift (3-7 nm) depends on structure TCC, structure of these dyes and about addition of compounds in an emulsion.

At formation of a hypsochromic J-band TCC under influence IV - IX the decrease of blue sensitivity AgBrI T-grains is observed. This decrease is higher in case of simultaneous addition in an emulsion of compounds. For compositions “X and TCC” the effect of supersensitization of emulsion sensitized TCC is observed on the “isolation” mechanism of supersensitization [4]. The influence of dyes III-VIII on spectral (red) sensitivity of emulsion depends on the order of addition in an emulsion TCC and III-IX.

Table 2: Spectral and photographic characteristices of emulsion sensitized TCC and their compositions with other dyes

N	Composition	Maximum of absorption of J-band TCC, nm	S red filter in %	DD
1	Dye I	645	100	2,2
2	Dye III, Dye I	633, 645	93	3
3	Dye IV, Dye I	634	47	3,5
4	Dye V, Dye I	627, 645	80	2,7
5	Dye V + Dye I	627	60	2,9
6	Dye VI, Dye I	624, 645	80	2,9
7	Dye VI + Dye I	620	40	3
8	Dye VIII, Dye I	632, 645	60	2,5
9	Dye VIII + Dye I	632	40	2,5
10	Dye IX, Dye I	645	80	2,4
11	Dye IX + Dye I	643	60	2,4
12	Dye X, Dye I	645	93	1,7
13	Dye X + Dye I	645	93	1,8
14	Dye II	651	100	1,9
15	Dye III, Dye II	647	100	2,1
16	Dye IV, Dye II	622	30	2,4
17	Dye V, Dye II	648	60	2,2
18	Dye V + Dye II	624, 640	30	2,4
19	Dye VI, Dye II	642	70	2,3
20	Dye VI + Dye II	625, 640	50	2,5
21	Dye VII, Dye II	645	100	2,1
22	Dye VII + Dye II	620, 640	40	2,3
23	Dye VIII, Dye II	648	90	2,2
24	Dye VIII + Dye II	620, 640	60	2,3
25	Dye IX, Dye II	651	70	2
26	Dye IX + Dye II	625, 645	50	2
29	Dye X, Dye II	651	120	1,5
30	Dye X + Dye II	651	110	1,5

The character of J-aggregation TCC at presence III-X is determined by the following factors: by a structure TCC, structure III-X, sequence of addition in an emulsion TCC and III-X. It is supposed that the basic contribution to interaction between dyes case the presence in molecules of the investigated dyes of heteronucleuses of an identical structure. At a combination TCC and thiamonomethincyanins the strong interaction between dyes (greatest hypsochromic shifts of J-bands TCC) is observed. For composition of dyes I+VI, different only in length of an outside polymethine chain the interaction is most effective. At a combination TCC and VIII in structure VIII there is only one identical on a structure with TCC heterocyclic nucleus (benzthiazole). Therefore interaction between dyes takes place to a lesser degree. For dyes TCC and IX in their structures there is only one blanket fragment - benzene ring - and the interaction between dyes takes place only at their simultaneous addition in an emulsion.

TCC and nullmethinmerocyanin X do not have identical aromatic heterocucles and the interaction between them do not take place at any sequence of addition of compaunds at an emulsion. Thus, for interaction of two dyes a necessary requirement is the presence in their structure of similar heterocyclic systems. The reason of various photographic activity of J-aggregates TCC can be a consequence of various oxidizing ability of holes (cations - radicals) TCC. Observed more effective bleaching of the latent image by hypsochromic J-aggregates TCC testifies to the greater oxidizing ability of holes TCC in such J-aggregates. It means, that the highest filled electronic level HOMO of molecules TCC in hypsochromic J-aggregates is located closer to a valence band AgBrI, than similar level in J-aggregates individual TCC. For monomethincyanins the level HOMO is located more closer to a valence band AgBrI. Such change of a position level HOMO can serve an indirect proof of existence on a surface AgBrI T-grains of mixed J-aggregate TCC, consisting from molecules TCC and molecules III-IX. In such J-aggregate the level HOMO of molecules TCC is displaced to a valence band AgBrI under influence included in structure of such J-aggregate of molecules III-IX. The decrease of sensitivity in a band of sensitization TCC is interlinked to the greater activity of an hole TCC. It is according to the mechanism of hole self-desensitization [4].

Hypsochromic shift of J-bands TCC and decrease of sensitivity of emulsion under influence III-IV are according to results obtained in [2] for an emulsion without chemical sensitization. Hence, the chemical sensitization do not render specific influence on interaction between TCC and III-IV.

Conclusion

1. The interaction between the elementary thiamonomethincyanins III-IV and TCC does not change at transferring from an emulsion without chemical sensitization to an emulsion with (S+Au) - chemical sensitization.
2. A necessary requirement of interaction is the presence in structure of both dyes of heterocycles (aromatic systems), similar on a structure.

The increase desensitizating of activity TCC in compositions with monomethincyanins III-IX is interlinked to a decreasing of position of the upper filled electronic level HOMO molecules TCC under influence monomethincyanine dyes. It can testify to formation of mixed J-aggregate TCC, which structure enter the molecules of monomethincyanins.

References

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Biography

Artem A. Fadeev. Graduated the Moscow Institut of Fine Chemical Technology of M.V. Lomonosov in 1997 on a speciality “Chemical technology of photographic materials”. The aspirant of termed institute and scientific worker of laboratory of black-and-white aerial photographic materials of FoMos PLC. The area of scientific interest included a scientific and application photography and spectral sensitization of photographic materials.