Russian Chemical Reviews **75** (5) 433 – 456 (2006) © 2006 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2006v075n05ABEH001208

Molecular assemblies of polymethine dyes

B I Shapiro

Contents

I.	Introduction	433
II.	Polymethine state of dyes	434
III.	Dye aggregation in solution	434
IV.	Dye aggregation on silver halide microcrystals	440
V.	Conclusion	453

Abstract. Aggregation processes of polymethine dyes in solutions and a heterogeneous system of AgHal microcrystals are considered. The mechanism of formation of nanoaggregates is discussed. The relationship between the aggregation and the structure of dye molecules is demonstrated. The aggregation is shown to depend on the composition and habit of AgHal microcrystals and the emulsion factors of real photographic systems. The structures and energy levels of aggregates are surveyed. The mechanism of photographic action of aggregates and ways of increasing their photochemical activity are discussed. The bibliography includes 272 references.

I. Introduction

Polymethine (cyanine) dyes became of practical interest after they have been used extremely successfully as spectral sensitisers of silver halide photographic materials. Spectral sensitisation was discovered by H Vogel more than 130 years ago.[1] It should be noted that Vogel was the first to demonstrate the uniqueness of polymethine dyes as spectral sensitisers. In spite of numerous attempts to employ other classes of dyes, only cyanines have found use in photographic technology.

In the course of development of spectral sensitisation, optimal polymethine dyes (Dy) were selected. Initially, dyes have been used primarily in the molecular (M) form. More recently, these dyes began to be used in the aggregated state. As demonstrated in numerous publications (see, for example, the reviews [2–6]), polymethine dyes capable of forming supramolecular structures, the so-called J-aggregates, have the highest photographic efficiency. Nowadays, most black-and-white and colour photographic materials are spectrally sensitised in the visible spectral region with J-aggregates of polymethine dyes.

The J-aggregation of polymethine dyes is a bright example of self-organisation of organic matter, which is somewhat similar to biological processes. Drawing the analogy between the dye aggregation and self-organisation in living matter, it should be noted that helical structures can also appear in the former case.[7] It should be emphasised that J-aggregation is a simpler phenomenon than self-organisation in living organisms, at least because molecules of the same (or related) compounds interact with each other, unlike genes or protein molecules whose helices contain different nucleotides or amino acids, respectively. Hence, the dye aggregation has attracted attention of researchers attempting both to understand general features of aggregation and to find application of the resulting self-organised systems. As mentioned above, some of these systems have long been in use in photographic processes.

Complicated organised structures of organic molecules (molecular assemblies) are of considerable interest primarily because such structures hold promise for processing and storage of large data sets. This phenomenon is used by nature. Reliable information libraries, such as DNA molecules in living organisms, are bright examples. It should be noted that biological self-organisation processes occur in aqueous solutions containing dissolved salts. Life originated from a salt solution of the primeval ocean. The present review shows that salts play an exceptionally important role also in the polymethine dye aggregation.

In the period of extensive development of optical methods for data recording and storage, molecular assemblies consisting of organic dyes have attracted considerable interest. Of all classes of organic dyes, polymethine dyes are distinguished by a high intensity of light absorption and tendency to aggregation.

It is commonly accepted that J-aggregation of cyanine dyes in solutions was virtually simultaneously discovered by Jelly [8] and Scheibe.[9] However, Sheppard has observed this phenomenon much earlier.[10, 11] He revealed systematic changes in the absorption curves of cyanine dyes in various solvents and found substantial changes in absorption in aqueous solutions. Jelly and Scheibe also found that absorption maxima are either shifted to shorter wavelengths (H-aggregation) or sharply shifted to longer wavelengths (J-aggregation) relative to the absorption maximum of the molecular form with increasing concentration of dye solutions.

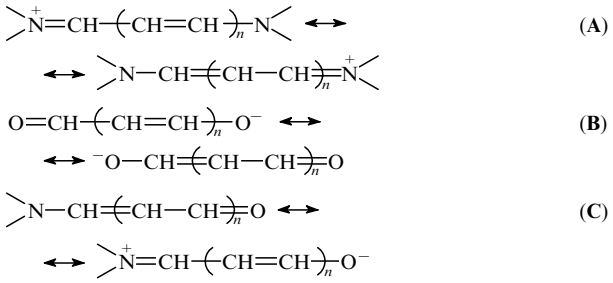
The J-aggregation process is most typical of polymethine dyes. Hence, before proceeding to problems of aggregation, it is worthwhile to consider the specific features of polymethine dyes, which distinguish these compounds from other classes of dyes both by the optical properties and tendency to self-organisation as highly ordered aggregates. The case in point is the so-called polymethine state associated with the specific structural features of polymethine dyes.

B I Shapiro Scientific Centre 'NIIKHIMFOTOPROEKT', Leningradsky prosp. 47, 125167 Moscow, Russian Federation. Fax (7-495) 258 75 98, tel. (7-495) 157 04 26, e-mail: bishapiro@mail.ru

Received 15 April 2005
Uspekhi Khimii **75** (5) 484 – 510 (2006); translated by T N Safonova

II. Polymethine state of dyes

Polymethine dyes (PMD) contain either of the following three main chromophoric systems: the amidinium ion (**A**), the carboxyl ion (**B**) and the bipolar amidic system (**C**)

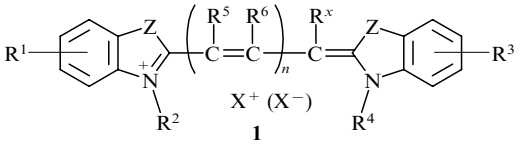


(**A**)

(**B**)

(**C**)

Schemes **A**–**C** show the limiting (resonance) structures of the chromophores. These π-conjugated systems are characterised by the presence of an odd number of methine groups between the charged polar atoms or groups.[2,3] Positively charged quaternary nitrogen atoms serve as such polar structural elements in amidinium-ion systems; negatively charged oxygen atoms, in carboxyl-ion systems. In formally neutral amidic systems, heteroatoms at the ends of the chromophoric system have opposite charges, *viz*., the positive charge on the quaternary nitrogen atom and the negative charge on the oxygen atom. Generally, the terminal nitrogen and oxygen atoms are involved in heterocyclic fragments, such as benzothiazole, benzoxazole, benzimidazole, quinoline, indolenine, rhodanine, thiohydantoin, *etc*. The formula of dyes of the amidinium-ion type can be represented as



1

Z = O, S, Se, NR, CH=CH (hereinafter, these dyes are referred to as oxa-, thia-, selena-, imida- and quinocyanines, respectively), *etc*.; R – R^x are different substituents; $n = 0-7$; X^+ (X^-) is a counterion.

What are the specific features of the polymethine state? The idea of the polymethine state was developed by Daehne.[12,13] This state substantially differs from other known states of π-conjugated systems, such as the polyene state containing an even number of methine groups and aromatic compounds also containing an even number of such groups. The polyene state is characterised by the equalisation of the π-electron density on the carbon atoms of the methine groups along the chain and the bond order alternation (single and double bonds); the aromatic state, by the equalisation of both the π-electron density and bond orders (one-and-a-half bonds). The ideal polymethine state is characterised by the alternation of the π-electron density on the polymethine chain and equal π-bond orders (nearly one-and-a-half bonds). These properties are retained in the photoexcited state of polymethine dyes, but the signs of the charges on the carbon atoms of the methine groups are reversed (Fig. 1).

The charge alternation along the chromophoric chain and charge inversion upon photoexcitation determine a high efficiency of light absorption in the visible and IR spectral regions due to an interaction with the dipole of the light wave. The molar extinction coefficients of cyanines are the largest among dyes [$\varepsilon = (2-3) \times 10^5$ litre mol^{-1} cm^{-1}].[3] In addition, the charge alternation in the ground state is responsible for considerable adsorbability of dyes on the ionic crystal surface, where the charge alternation also occurs.[3]

Due to the bond order equalisation in the polymethine chain of dyes resulting in the presence of nearly one-and-a-half bonds, the molecules are rigid and planar. X-Ray diffraction data for

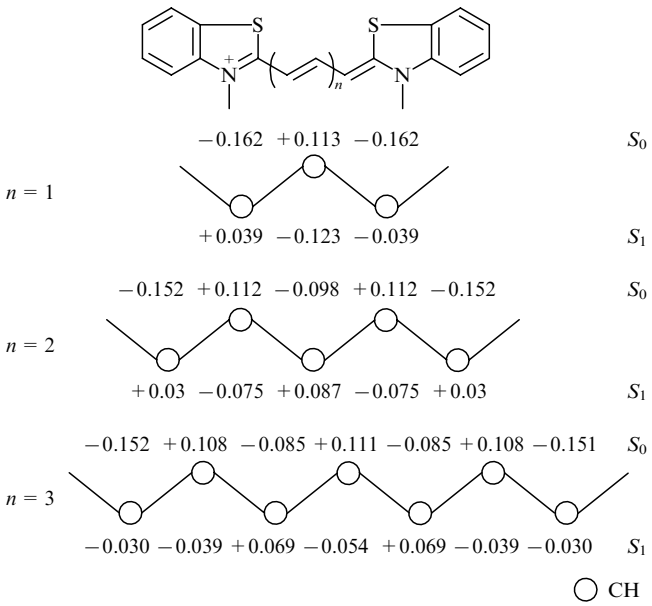


Figure 1. Diagrams of the π-electron density distribution in the polymethine chain of thiapolymethinecyanines in the ground (S_0) and first photoexcited (S_1) states.
Calculations by the Pariser – Parr – Pople method.[14]

symmetrical dyes confirm this conclusion.[3] Most of the molecules of typical cyanines are almost planar (angles between the planes of the heterocycles are smaller than 15°). The rigid planar structure of cyanines is responsible for the appearance of narrow absorption bands. The planarity of polymethine dye molecules is a prerequisite for the 'plane-to-plane' aggregation with a particular shift angle of molecules relative to each other, thus providing an optimal interaction between the oppositely charged methine groups.

III. Dye aggregation in solution

Aggregation of cyanine dyes in aqueous solutions can be exemplified by 1,1′-diethyl-2,2′-cyanine chloride studied in depth (Fig. 2).[2,15]

The absorption spectrum of a very dilute solution of the dye (curve *1*) is virtually identical to the spectrum of an ethanolic solution containing the main maximum at 525 nm and an additional maximum at 490 nm. This spectrum corresponds to individual solvated molecules (M form), which do not interact with each other. A new maximum of the dimer (D) shifted to shorter wavelengths appears and the intensity of the molecular M band decreases with increasing dye concentration in an aqueous solution (curve *2*). Such changes were observed for many classes of dyes, including cyanines, merocyanines, triphenylmethane, xanthene, rhodamine, *etc*. dyes.[16] The further aggregation (after the formation of dimers) leads to a hypsochromic shift of the band maximum with respect to the dimer band and its widening (curve *3*). This spectral change is related to the formation of polymolecular aggregates, which are called H-aggregates (Hypsochromic), and the corresponding absorption bands are called H-bands.

If the dye concentration is higher than the concentration at which H-aggregation starts, the absorption spectrum shows an intense very narrow band described by Jelly and Scheibe.[8,9] The maximum of this band at 573 nm is bathochromically shifted relative to the M-band (curve *4*). The new band was named the J-band after Jelly, and the corresponding aggregation state was called the J-state. It is commonly accepted that a J-aggregate is a polymolecular state in which planar dye molecules are packed together in a plane-to-plane fashion. In the resulting aggregate, a

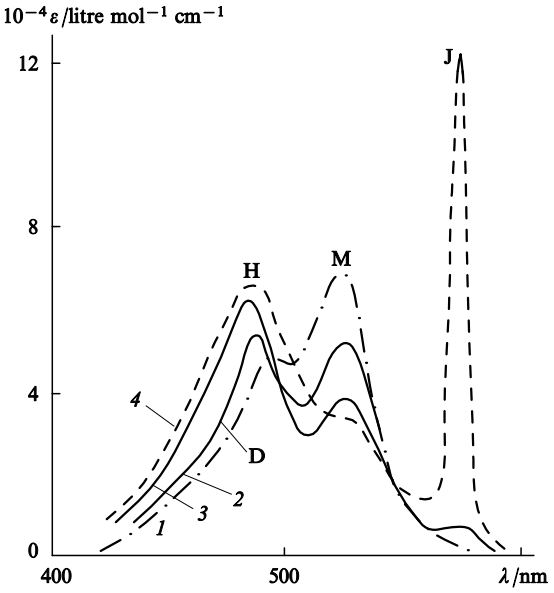


Figure 2. Absorption spectra of aqueous solutions of 1,1′-diethyl-2,2′-cyanine chloride.[2]
The concentrations of the solution at 25 °C /mol litre^{-1}: (*1*) 1.3×10^{-5}, (*2*) 1.3×10^{-3}, (*3*) 7.1×10^{-3}, (*4*) 1.4×10^{-2}.

common π-electron system is present, which is manifested in a bathochromic shift of the absorption band, a decrease in its width and, consequently, an increase in intensity. Absorption in the J-band region is due to the cooperative action of all molecules involved in the aggregate, and the absorbed energy is distributed throughout the aggregate. This process is typical of the exciton motion, *i.e.*, the transfer of the excited state, which is formed upon light absorption by one molecule in the close-packed aggregate, from one molecule to another in a time shorter than the oscillation period of the dye. The aggregation of cyanines in solution was reviewed in detail by Herz.[16,17]

It is worthwhile to consider the spectroscopic manifestation of interactions between molecules in aggregates in terms of McRae–Kasha's model[18,19] for a dimer as the simplest case. The probability of the electron transition from the ground state (*G*) to the excited state (*E*) split due to an intermolecular interaction depends on the angle α between the direction of the transition dipole moments and the axis of the aggregate (the axis through the centres of the molecules in the aggregate, see Fig. 3). For $\alpha = 90^\circ$, the spectral transition to the higher split excited state is most probable. This corresponds to sandwich-type dimers of cyanine dyes characterised by an absorption band hypsochromically shifted relative to the M-band. The transition to the lower split state is forbidden. If $\alpha = 0^\circ$, the transition to the lower split excited state is preferable, which corresponds to a bathochromic shift of the absorption band of the dimer. In the general case, for example, at $\alpha > 54^\circ$, the transition to the higher split state with a hypsochromic shift of the absorption band is more probable. For $\alpha < 54^\circ$, the transition to the lower split state with a bathochromic shift is preferable.

This model was extended to larger aggregates (H- and J-aggregates). Based on X-ray diffraction data and results of calculations for aggregates of cyanine dyes, it was concluded that the structural parameter, *viz.*, the packing angle in the aggregate, is of most importance for the spectral properties of such aggregates.[3,20,21]

The structure of an aggregate can be pictorially represented as a deck of cards (Fig. 4). The shift angle in a slipped deck of cards is the above-mentioned packing angle determining the spectral absorption of the aggregate. Calculations demonstrated that $\alpha = 60^\circ$ corresponds to H-aggregates, whereas $\alpha = 30^\circ$ and 19° correspond to J-aggregates. The smaller the angle α, the larger the bathochromic shift of the absorption band of J-aggregates.

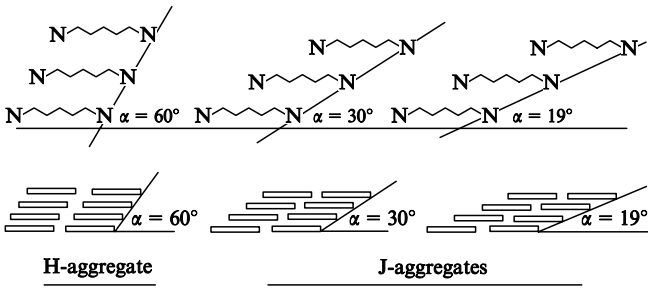


Figure 4. Schematic representation of the structures of H- and J-aggregates of cyanine dyes;[6]
α is the packing angle of the aggregate.

The two-dimensional structure of J-aggregates considered by Kuhn, the so-called brickwork structure with the packing angle $\alpha = 19^\circ$ (Fig. 5 *a*), is substantiated the most.[21–24] Calculations by the molecular orbital (MO) method demonstrated that 3–5 cyanine molecules are sufficient for the appearance of the J-band in the absorption spectrum of a brickwork structure.[20,25,26]

It should be noted that the aggregation of some dyes, for example, of *meso*-methyl-substituted thiacarbocyanines, (particularly, on silver halides) is characterised by double absorption bands. One peak is hypsochromically shifted relative to the M-band, whereas another peak of approximately equal intensity is shifted bathochromically. For such aggregates, a herringbone structure is considered (Fig. 5 *b*).[27] In the latter, dimers of the dye serve as the main structural units, which are repeated (translated)

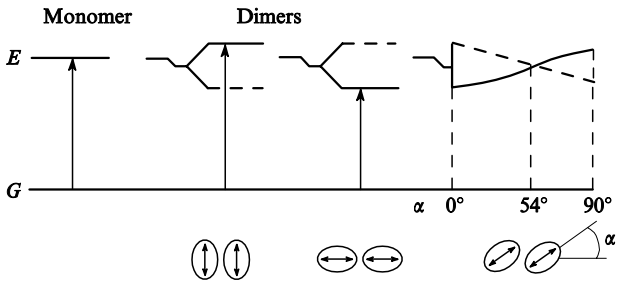


Figure 3. Diagram of the energy levels of the monomer of the dye and its dimers depending on the angle between the direction of transition dipole moments and the axis of the aggregate;[18,19]
G is the ground state, *E* is the excited state.

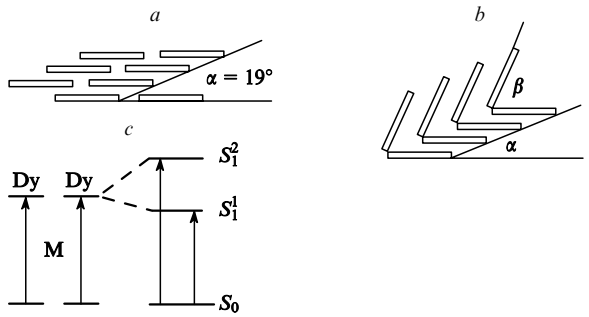


Figure 5. Brickwork (*a*) and herringbone structures (*b*) of J-aggregates and the scheme of energy level splitting in dimeric fragments of the aggregates (*c*).[27]

many times. Due to splitting of the energy levels of the dye in the dimer (according to Davydov), two spectral transitions occur (Fig. 5 *c*). The intensity ratio of these transitions is determined by the angles α and β.[27] For $\beta = 90^\circ$, two transitions have equal intensities.

A dimer is the simplest dye aggregate. The formation of dimers was described in early publications (see, for example, the review [16]). Dimers are formed by cyanines containing polymethine chains with different lengths (dyes **1**, $n = 0-3$). The formation of dimers from anionic monomethinecyanines has also been documented.[28–30] The M- and D-forms are in thermodynamic equilibrium. This is exemplified by thiacyanine ($n = 0$) in Fig. 6. The intensity of the M-band increases, whereas the intensity of the D-band decreases with decreasing dye concentration and increasing temperature, the curves passing through an isosbestic point.

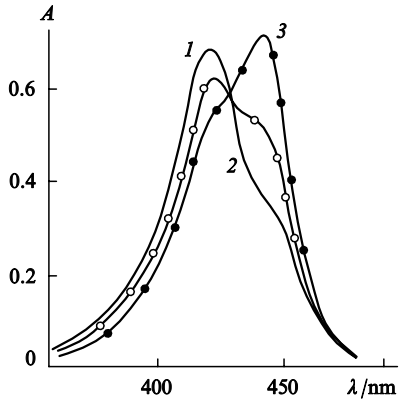


Figure 6. Absorption spectra of aqueous solutions of the triethylammonium salt of 5,5′-dichloro-3,3′-di(γ-sulfopropyl)thiacyanine;[28]
A is the optical density; the concentration of the solution /mol litre^{-1}: (*1*) 1×10^{-5}, (*2*) 1×10^{-6}, (*3*) 1×10^{-7}; the cell length /cm: (*1*) 0.1, (*2*) 1.0, (*3*) 10.

Van der Waals forces and dispersion interactions of π-conjugated systems play the major role in the formation of dimers.[16] Dimerisation of cyanines was studied in detail by West and Pears.[31] It was found [17, 31] that dimerisation in aqueous solutions increases with increasing length of the polymethine chain and with increasing hydrophobicity due to elongation of *N*-alkyl substituents and, on the contrary, dimerisation decreases with increasing degree of non-planarity of dye molecules, in particular, due to bulky substituents. The free energy of dimerisation of cationic cyanines changes only slightly (by 5–7 kcal mol^{-1}).[31] For anionic dyes containing sulfoalkyl groups at the nitrogen atoms in heterocyclic moieties, the changes in the free energy of dimerisation are larger.[28] Apparently, stability of dimers of anionic cyanine dyes is determined by a strong intermolecular Coulombic interaction between the sulfo group of one molecule and the positive charge on the chromophore of another molecule. The possibility of formation of mixed dimers containing cationic thiacarbo- and dicarbocyanines in aqueous solutions was discussed.[31]

It should be noted that the formation of dimers in aqueous solutions leads to fluorescence quenching with a simultaneous increase in the role of triplet states.[16] The only exception is dimers of oxacyanine, which exhibit stronger fluorescence in solutions compared to its monomers.[32] Apparently, this is associated with the difference in the structure of two isomers of cyanines involved in the dimers.

Larger aggregates, *viz*., trimers, tetramers and *n*-mers, including H-aggregates (Fig. 7), are formed as the dye concentration of in solution increases and the temperature decreases,[33] the hypsochromic shift of the absorption band of aggregates being increased. As a rule, H-aggregates, like dimers, show no luminescence. However, the appearance of narrow H-bands (H*) was observed.[34] Colloidal particles can be H*-aggregates exhibiting strong luminescence.[33, 34]

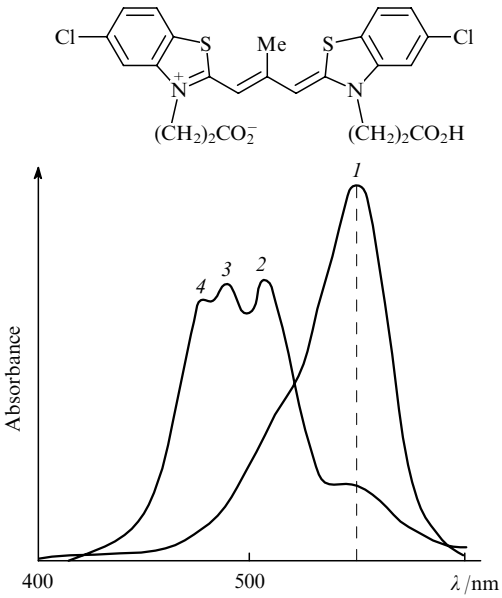


Figure 7. Absorption spectra of different forms of thiacarbocyanine in aqueous solutions at different concentrations and temperatures;[33]
(*1*) a monomer, (*2*) a dimer, (*3*) a trimer, (*4*) a tetramer.
The concentration of the solution /mol litre^{-1}: (*1*) 2×10^{-6}, (*2–4*) 2×10^{-4}; the temperature /°C: (*1*) 60, (*2–4*) 5.

The J-aggregation of cyanine dyes is of particular interest. Most earlier studies investigated cationic dyes. The formation of J-aggregates from individual molecules occurred. This process was poorly controlled and led to the uncontrolled growth of J-aggregates up to the formation of colloidal particles.[16, 17] The results of investigation of J-aggregation of imidacarbocyanine molecules performed by Herz [16, 17] are presented in Fig. 8 as an example.

Equilibria between the monomeric and aggregated forms of dyes can be studied by analysing absorption spectra at different dye concentrations. According to the law of mass action, the equilibrium between the monomeric and J-aggregated forms can be written as follows:[16]

$$n\, c_{\mathrm{M}} \rightleftharpoons c_{\mathrm{J}}\,, \tag{1}$$

$$K = \frac{c_{\mathrm{J}}}{c_{\mathrm{M}}^{n}}\,,$$

$$\log(nc_{\mathrm{J}}) = \log(nK) + n \log c_{\mathrm{M}}\,, \tag{2}$$

where n is the number of monomers in the J-aggregate and K is the equilibrium constant. The plot of $\log(nc_{\mathrm{J}})$ *vs.* $\log c_{\mathrm{M}}$ should be linear with a slope of n. The change in the free energy of aggregation is determined from the temperature dependence of K.

For imidacarbocyanine in an aqueous electrolyte solution, $n = 4$.[16, 17] Herz hypothesised [16] that, under experimental conditions, colloidal particles can be formed, and $n = 4$ corresponds to the single spectroscopic unit rather than to the size of J-aggregates. The same value of n was obtained for the J-state of cationic naphthothiacarbocyanine [25] in an aqueous solution and for 1,1′-diethyl-2,2′-cyanine.[35] Small values of n were determined from spectroscopic data in some other studies.[16] It should be noted that irreversibility of the equilibrium in a monomer–J-aggregate system is the main problem in determining the number of molecules in J-aggregates and the thermodynamic parameters of aggregation. Generally, small J-aggregates (consisting of a few molecules) grow into colloidal particles. The identification of

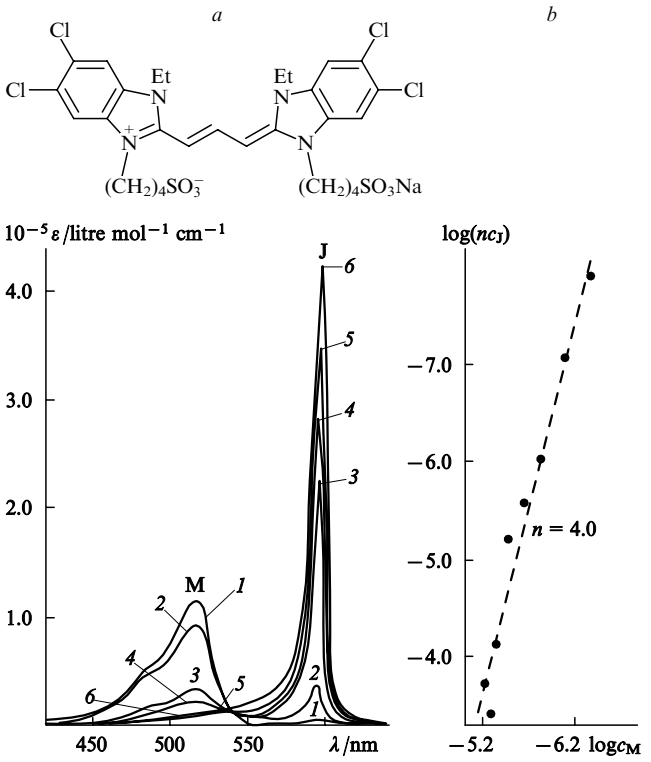


Figure 8. Dependence of absorption of benzimidacarbocyanine at 25 °C on its concentration in a 10^{-3} M NaOH aqueous solution.[16]
The concentration of the solution /mol litre^{-1}: (*1*) 0.5×10^{-6}, (*2*) 1.0×10^{-6}, (*3*) 5.0×10^{-6}, (*4*) 1.0×10^{-5}, (*5*) 1.0×10^{-4}, (*6*) 4.0×10^{-4}; c_M and c_J are the concentrations of the monomeric and aggregated forms of the dye, respectively.

states by spectroscopic methods is complicated by the fact that particles of different sizes give similar absorption maxima. Hence, reversibility of the equilibrium and colloidal stability of solutions in time are the main criteria in the determination of the state of dyes.

A new method of J-aggregation (from dimers rather than from individual molecules) was examined in the studies.[36,37] This method typical of anionic cyanine dyes is referred to as the block construction of aggregates.[37] The equilibrium between dimers and J-aggregates of the pyridinium salt of 3,3′-di(γ-sulfopropyl)-4,5,4′,5′-dibenzo-9-ethylthiacarbocyaninebetaine is illustrated in Fig. 9. It can be seen that the equilibrium is thermodynamically reversible because the spectral curves pass through an isosbestic point. The tendency of dyes to aggregation is enhanced with decreasing temperature and increasing concentration. These results are consistent with the characteristic features of aggregation of thiacyanines.[28,36]

To determine the sizes of J-aggregates, the plot of log(nc_J) *vs.* logc_D was constructed (Fig. 10). The slope of the line [corresponding to the number (*m*) of dimers in the J-aggregate] is 2, *i.e.*, the J-aggregate consists of two dimers or four monomers. Probable structures of J-aggregates formed from two dimers are shown in Fig. 11.[21–23] In all cases, the formation of J-aggregates from dimers is associated with the shift of the molecules in dimers with respect to each other. It was hypothesised that a brickwork structure is most preferable. It was demonstrated that J-aggregates of thiacyanine [triethylammonium salt of 5-chloro-3,3′-di(γ-sulfopropyl)-4′,5′-benzothiacyaninebetaine] also consist of two dimers, *i.e.*, of four dye molecules.[36]

In studies of the equilibria between different forms of anionic thiacyanine dyes in aqueous solutions the following, at first glance, paradoxical conclusion was reached: the block construction of J-aggregates from dimers is the most preferable method for

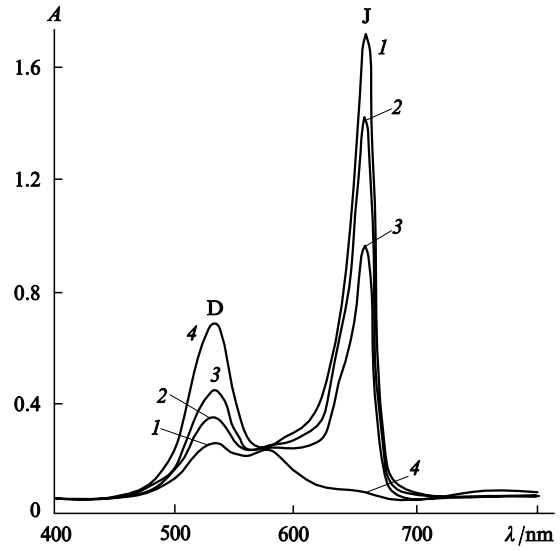


Figure 9. Absorption spectra of thiacarbocyanine in aqueous solutions. The concentration of the solution /mol litre^{-1}: (*1*) 10^{-4}, (*2*) 3.3×10^{-5}, (*3*) 1×10^{-5}, (*4*) 0.5×10^{-5}; the cell length /cm: (*1*) 0.1, (*2*) 0.3, (*3*) 1.0, (*4*) 2.0.

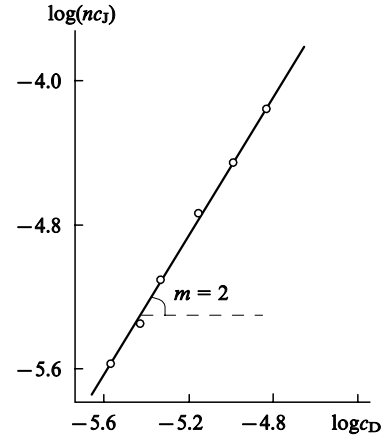


Figure 10. Plot of log(nc_J) *vs.* logc_D for thiacarbocyanine.

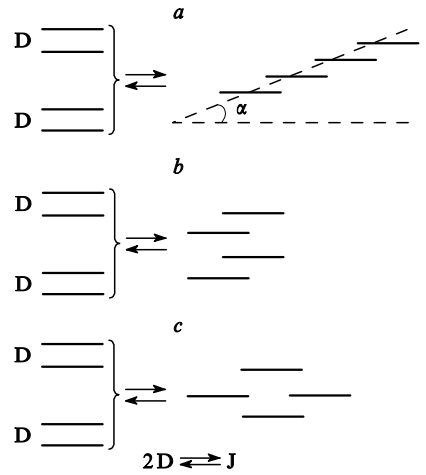


Figure 11. Schemes of formation of J-aggregates of the slipped-deck-of-cards (*a*), ladder (*b*) and brickwork (*c*) types from dimers.

the construction of 'ideal' J-aggregates of the same size (monostructural J-aggregates). This new approach to the construction of J-aggregates was used for the preparation of mixed J-aggregates from dyes containing polymethine chains of different lengths.[37, 38] To our knowledge, Scheibe *et al.*[39] observed for the first time the appearance of new bands in the absorption spectrum of a system consisting of two dyes, *viz.*, 1,1′-diethyl-2,2′-cyanine and its 2-benzoselenazole analogue. In the spectrum of a complex mixture of solvents, benzene – amyl alcohol – water, an additional absorption band was found between the bands of J-aggregates of individual dyes. The appearance of new bands for analogous dyes containing long alkyl groups in the spectra of Langmuir – Blodgett films was described by Penner and Mobius.[40] Mixed amalgam-type aggregates were obtained [41] in Langmuir – Blodgett films for 3,3′-diethyl-9-phenylthiacarbocyanine dyes substituted in heterocycles. It should be noted that J-aggregates composed of two types of dyes were formed in heterogeneous systems at the water – organic solvent interface.

The main scheme of the block construction of J-aggregates from molecules of different dyes in water involves the preliminary formation of dimers of these dyes due to a shift of the J-aggregate $\rightleftharpoons$ dimers equilibrium toward the dimers (upon heating of their solution) followed by the formation of complex aggregates (upon cooling of the systems).[37, 38] The absorption spectrum of a mixture consisting of solutions of thiacarbocyanine and thiadicarbocyanine is a summary curve of the bands of the starting dyes (Fig. 12, curve *1*). Heating of the solutions to 50 – 80 °C leads to destruction of J-aggregates of individual dyes and the appearance of bands corresponding to absorption of dimers of dyes (see Fig. 12, curve *2*). After subsequent cooling of the solutions, the dimers form new J-aggregates including different molecules (see Fig. 12, curve *3*). The absorption band of mixed J-aggregates appears at longer wavelengths compared to the band of J-aggregates of thiacarbocyanine and is hypsochromically shifted relative to the absorption band of J-aggregates of thiadicarbocyanine. This phenomenon is common to thiacyanines, which can form J-aggregates in aqueous solutions and contain an extensive π-conjugated system in the heterocycles. Therefore, mixed aggregates with desired spectral properties can be prepared by choosing appropriate pairs of dyes.

Apparently, the resulting mixed J-aggregates are homogeneous structures analogous to solid solutions of dyes, which is confirmed by the character of their fluorescence spectra. Intrinsic luminescence bands (Fig. 13 *b*) correspond to individual absorption bands of J-aggregates of the starting dyes and their mixture (Fig. 13 *a*). Therefore, the block construction of J-aggregates in solution is an efficient method for the preparation of J-aggregates of cyanine dyes containing polymethine chains with different lengths and mixed J-aggregates. Hence, this method can be considered as a promising approach to the formation of complex organised structures, *viz.*, molecular assemblies with new optical properties.

A different type of aggregates composed of dimers was obtained in studies of cyanine dyes, which substantially differ in the length of the polymethine chains, *viz.*, thiacyanines and thiadicarbocyanines.[42] In this case, mixed J-aggregates are not formed, absorption bands of dimers of thiadicarbocyanines disappear and the absorption spectra show new absorption bands. This is illustrated in Fig. 14, which shows the absorption spectra

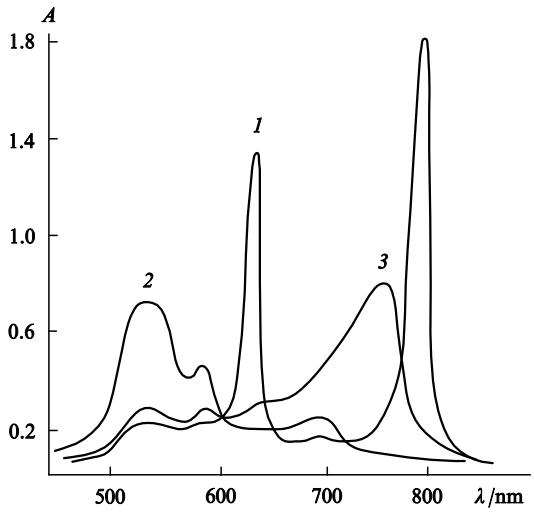


Figure 12. Absorption spectra of a 1 : 1 mixture of aqueous solutions of thiacarbocyanine and thiadicarbocyanine ($c = 1 \times 10^{-4}$ mol litre^{-1}) after mixing at 20 °C (*1*), upon heating to 50 °C (*2*) and after cooling to room temperature (*3*).[37, 38]

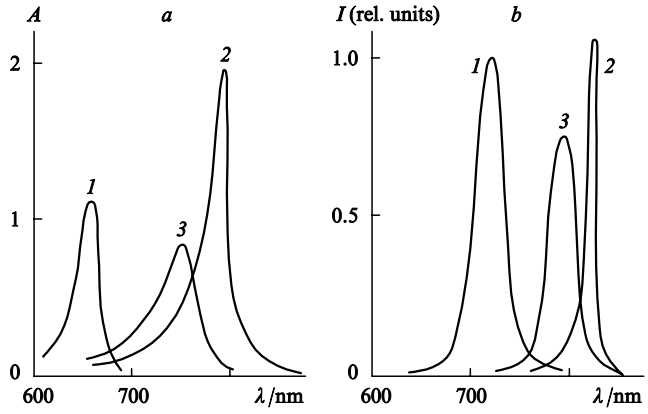


Figure 13. Absorption spectra (*a*) and fluorescence spectra (*b*) of J-aggregates of thiacarbocyanine (*1*) and thiadicarbocyanine (*2*) and their mixture (*3*) in aqueous solutions.[37, 38]

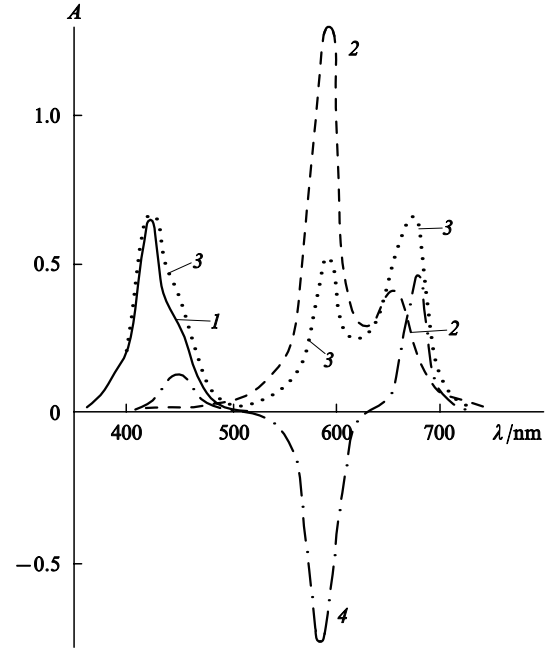


Figure 14. Absorption spectra of aqueous solutions of triethylammonium salts of 5′-chloro-3,3′-di(γ-sulfopropyl)-4,5-benzothiacyanine (*1*) and 3,3′-di(γ-sulfopropyl)-9,11-(β,β-dimethyltrimethylene)-10-methylthiadicarbocyanine (*2*) and their mixture (*3*) at room temperature.[42]
The concentration of the dyes $c = 1.0 \times 10^{-5}$ mol litre^{-1}; (*4*) the difference spectrum of the starting dyes and their mixed solutions.

of aqueous solutions of triethylammonium salts of 3,3′-di(γ-sulfopropyl)-4,5-benzo-5′-chlorothiacyanine and 3,3′-di(γ-sulfopropyl)-9,11-(β,β-dimethyltrimethylene)-10-methylthiadicarbocyanine. The thiacyanine existed in the dimeric (λ_{max} = 421 nm) and monomeric (λ_{max} = 442 nm) forms (curve *1*). The thiadicarbocyanine also existed in the dimeric (λ_{max} = 588 nm) and monomeric (λ_{max} = 655 nm) forms (curve *2*). Curve *3* represents the absorption spectrum of mixed equimolar solutions of the dyes. After mixing of solutions of the dyes, the intensity of the dimer band of the thiadicarbocyanine substantially decreases and new absorption bands appear at λ_{max} = 444 and 678 nm, which is shown by curve *4* (obtained by subtracting curves *1* and *2* from curve *3*). This interaction between thiacyanines and thiadicarbocyanines has a general character regardless of the nature of substituents in the heterocyclic moieties of the dyes.[42] Therefore, interaction between dimers of two dyes is pronounced. It was hypothesised that this is associated with the presence of dimer(1)–dimer(2) interactions involving different dyes. Apparently, splitting of the dimer band of the dicarbocyanine dye is due to splitting of the electron levels of the dimer in a 'heterocontact dimer' due to the perturbing action of the dimer of the thiacyanine dye. It was concluded that the formation of 'heterocontact' aggregates is energetically more favourable than the formation of dimers and J-aggregates of individual dyes. Therefore, in this case, as in the case of formation of mixed J-aggregates, dimers are the main building blocks of organised polymolecular structures. However, the formation of mixed J-aggregates is, apparently, hindered due to a substantial difference in the geometry of the interacting molecules and, consequently, the so-called suprastructures with incommensurate elements are formed.[43]

The influence of electrolytes and surfactants on aggregation of cyanines was examined in several studies (see, for example, Refs 16, 20 and 44). It is evident that the aggregation of charged cyanine dye molecules is influenced by electrolytes. Generally, the introduction of inorganic electrolytes stimulates aggregation.[16] This is related to the salting out of the dye from a solution under the action of an electrolyte. The charge of the ion opposite to the charge of the dye molecule plays a great role. In aqueous solutions of anionic dyes,[45] the electrolyte concentration stimulating aggregation decreases and the J-aggregation rate increases with increasing charge of the cation.† It was hypothesised that the self-aggregation becomes more probable in the presence of framework-forming auxiliary partners (for example, ions). Figuratively speaking, ions can serve as 'nails' facilitating the building of J-aggregates. In addition, ions involved in J-aggregates can promote their stabilisation.

Organic surfactants (unlike inorganic electrolytes) hinder the self-association of dyes in water.[46] This influence is characteristic also of micelle-forming non-ionic surfactants.[16] This property lies at the basis of the spectroscopic method for the determination of the critical micelle concentration. It should be emphasised that dye aggregation can, on the contrary, occur in the pre-micellar region of surfactant concentrations.

The influence of surfactants on aggregation was examined.[7, 47–50] The presence of long hydrocarbon fragments at the nitrogen atoms in the imidacarbocyanine molecule is found to favour the formation of helical structures of J-aggregates, in which the hydrocarbon tails serve as a framework at which a helical packing of the dye molecules is assembled as a nanotube. An example of such structures characterised by a two-band spectrum of the J-aggregate is shown in Fig. 15.[50]

Unlike the deaggregating action of micelle-forming surfactants, polymeric surfactant ions (polyelectrolytes) stimulate aggregation. The spectral shifts caused by interactions of polyelectrolytes with both anionic and cationic dyes were studied in detail (see references in the review [16]).

† See also the publication by T D Slavnova, A K Chibisov, H Gorner *J. Phys. Chem. A* **109** 4758 (2005).

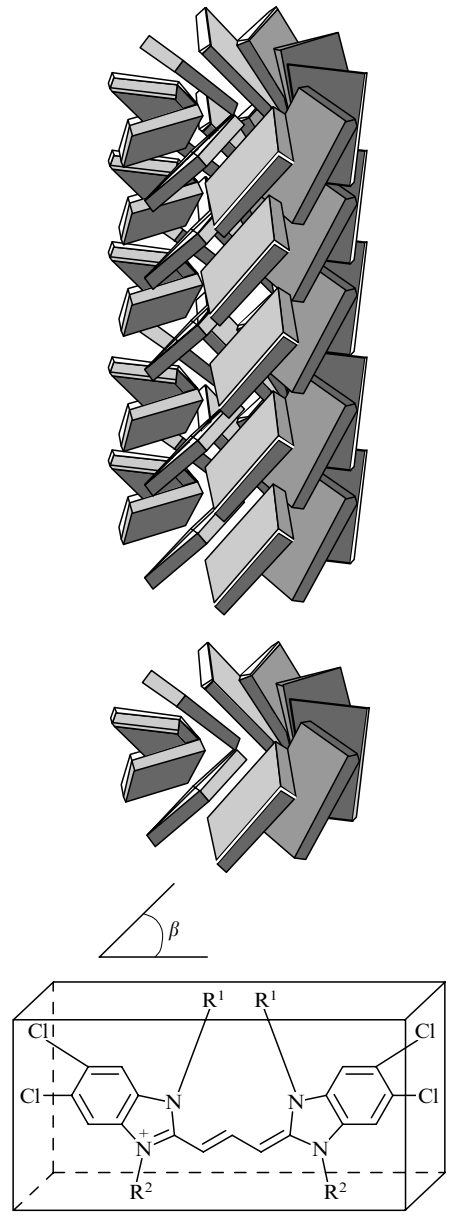


Figure 15. Cylindrical model of the helical structure of imidacarbocyanine.[50]

The influence of gelatine on aggregation of cyanine dyes in solutions was studied in depth. The appearance of a new band at longer wavelengths after the addition of traces of gelatine to aqueous solutions of carbocyanines was observed for the first time by Sheppard [51] and Solovev.[52] More recently, Dickinson,[53] Borin [54] and Boyer *et al.*[55] performed systematic studies of the influence of the gelatine concentration, the temperature and pH on aggregation of cationic dyes in aqueous gelatine solutions. It was found that J-aggregation of dyes is initiated in the presence of a small amount of gelatine (~ 0.01%), and a further increase in the gelatine concentration in solution leads to destruction of J-aggregates to give monomers. In a 1% gelatine solution, J-aggregates are absent. In addition, pH of an aqueous gelatine solution should be higher than pH of the isoelectric point of gelatine. It should be noted that the solutions contained not only J-aggregates but also other 'short-wavelength' aggregates of dyes. More recently, Hermel and Seeboth [56] studied the influence of the molecular mass distribution of gelatine and the effect of liquid-crystalline *N*-substituted butylaniline on aggregation of oxacar-

bocyanine. Krasovskii *et al.*[57] investigated the properties of the anionic analogue of this dye containing sulfopropyl groups at the nitrogen atoms in aqueous solutions near the gel-formation threshold of gelatine. It was found that J-aggregates are more readily formed in low-molecular-weight gelatines. However, mixtures of monomeric and several aggregated forms (dimers, H- and J-aggregates) were obtained in these systems as well. It was demonstrated [51, 52] that traces of gelatine act as aggregation centres because adsorption of dyes occurs on particular groups of gelatine.

Gelatine was demonstrated [58] to promote J-aggregation of anionic dyes from dimers according to the mechanism of block construction. In this case, gelatine serves as the third component facilitating aggregation.

A study of the dependence of J-aggregation on the type of gelatine showed [59] that the aggregation is substantially influenced by the positively and negatively charged groups. In acidic gelatines, J-aggregation occurs much more readily than in alkaline gelatines. In acidic gelatines containing positively charged quaternary nitrogen atoms at a pH under study, J-aggregation starts at higher temperatures and lower gelatine concentrations. J-Aggregation is slowed down as the number of acidic groups in the gelatine molecule increases. It was concluded that the quaternary nitrogen atoms in acidic gelatines serve as J-aggregation centres of anionic dyes. The ability of gelatine to catalyse J-aggregation was exploited for the preparation of gelatine layers containing nanoparticles of J-aggregates consisting of several dye molecules.

In recent studies, considerable attention was given to the formation of J-aggregates in films of various polymers, including electroconducting polymers. Composites containing J-aggregates are promising materials for the construction of electroluminescent displays and the preparation of electrorefractive layers, nonlinear optical systems and other systems used in nanoelectronics. Mal'tsev *et al.*[60–62] investigated J-aggregates as a light-emitting medium in electroconducting polymers. The authors observed electroluminescence of J-aggregates of mono-, tri-, penta- and heptamethinecyanines in the visible and IR spectral regions. The photoelectrical, nonlinear optical and photorefractive properties of J-aggregates in polyimide films were investigated.[63, 64] The nonlinear optical properties of J-aggregates of thiacarbocyanine dyes in multilayer polymer films were studied.[65] Films containing J-aggregates of cyanine dyes were used for generation of ultrashort laser pulses and nonlinear optical transformations.[66–70] The J-aggregation of thiacarbocyanine dyes in polymer films was investigated.[71] Data on J-aggregation in polymeric matrices were obtained primarily for pseudoisocyanine in polyvinyl alcohol,[72, 73] polystyrene sulfonate and polyacrylic acid.[74–76]

IV. Dye aggregation on silver halide microcrystals

The most detailed information on aggregation of cyanine dyes was obtained in long-term studies of spectral sensitisation of AgHal-based photographic materials. It is known that J-aggregation more readily occurs at the AgHal/solution interface.[2, 16] The use of cyanine dyes for spectral sensitisation of photographic silver halide emulsions provides a substantial increase in additional light sensitivity in the region, where AgHal microcrystals do not absorb light. Dyes capable of forming supramolecular structures, *viz.*, J-aggregates, are characterised by the highest photographic efficiency.[2–6, 77]

The J-aggregation process is determined primarily by the molecular structure of the dye (the lengths of the polymethine chain, the structure of heterocyclic rings and the presence of substituents in these moieties and in the chain), the nature of the halogen atom, the habit and size of emulsion microcrystals, the presence of ions and compounds adsorbed on AgHal (stabilisers, surfactants, colour-forming components, *etc.*), pBr and pH.[2, 3, 16, 17, 20, 77, 78]

The J-aggregation by itself is not a sufficient condition for high efficiency of spectral sensitisation. Many J-aggregating dyes are inefficient under particular conditions. The photographic efficiency of J-aggregates cannot be attributed only to a change in the position of the energy levels of dye molecules upon J-aggregation. The experience showed that the surface state of AgHal microcrystals and the topography of impurity centres play a decisive role. The surface defects and impurity centres are of importance in J-aggregation and location of photogenerated electrons and holes. Interactions between J-aggregates of a dye and impurity sites can lead to a decrease in the photographic activity of the dye. Generally, this is attributed to desensitisation and self-desensitisation of dyes.[79, 80] Desensitisation causes a decrease in the intrinsic (blue) light sensitivity of AgHal. Self-desensitisation leads to a decrease in the light sensitivity in the absorption zone of dyes. The efficiency of spectral sensitisation can substantially be increased by introducing supersensitisers (compounds, which inhibit or completely exclude self-desensitisation of dyes).

1. Relationship between aggregation and the structure of dyes

The relationship between the structure of dyes and their tendency to form aggregates in solutions and on the surface of AgHal were studied in depth (see references in the publications [2–6, 77–80]). The available data are rather contradictory due to complexity of a photographic system.

Among cyanine dyes unsubstituted in heterocyclic fragments and the outer polymethine chain, mono- and trimethinecyanines are most prone to aggregation on the surface of AgBr(I) emulsion grains.[2, 3, 77] Generally (with rare exception [81–83]), di- and tricarbocyanines (penta- and heptamethinecyanines) form H-aggregates rather than J-aggregates on AgHal substrates.[17, 77] This may be related to the requirements of a highly ordered arrangement of molecules in J-aggregates, whereas the uniformity of the states of the molecules is less probable due to an increase in the number of *cis–trans* isomers with increasing length of the polymethylene chain of dyes.[84] As a result, any deviation from the uniformity of structural elements, in particular, due to *cis–trans* isomerism, hinders aggregation. For example, only rigid fixation of the chain by polymethylene bridges in thiadi- and -tricarbocyanine molecules preventing *cis–trans* isomerism results in J-aggregation of dyes containing such a long polymethine chain in solutions and on AgHal.[37, 38, 83, 85]

Derivatives of partially hydrogenated rings (thiazoline and pyrrolidine) show almost no tendency to form J-aggregates. Analogous dyes containing conjugated heterocyclic fragments (thiazole and 1,3,4-thiadiazole) have a weak tendency to form aggregates, whereas this tendency is substantially stronger in the case of compounds containing fused heterocyclic systems with a high degree of π-electron delocalisation (such as benzoxazole, benzoselenazole, benzothiazole, quinoline, *etc.*). J-Aggregation in AgHal emulsions accompanied by a shift of absorption bands to longer wavelengths increases in the thiazoline < thiazole < benzothiazole < naphthothiazole series. This indicates that interactions of π-electrons in heterocyclic systems play a considerable role in the formation of polymolecular states. The phenyl groups in the thiazole or thiadiazole moieties have an analogous effect on J-aggregation.[77] Indo- (see Ref. 78) and imidacarbocyanines,[86] as well as indo- and thiadiazolo-1,3,4-dicarbocyanines,[77] also show a tendency to form J-aggregates.

Merocyanines rarely form J-aggregates on AgHal, although dimethinemerocyanines containing indolenine and pyrazolone moieties and malonodinitrile derivatives [84] give J-bands in emulsions. Sensitisation and absorption spectra of a number of dimethinemerocyanines, derivatives of unsymmetrical cyclic compounds (in particular, 3-alkylrhodanine and 1,3-dialkylthiohydantoin), show J-bands whose intensity increases with increasing duration of storage of melted sensitised emulsions.[77]

The introduction of substituents into different classes of dye molecules has a similar effect on their aggregation. For example, J-aggregation is substantially enhanced in the presence of chlorine atoms in heterocyclic fragments of various carbocyanines or the

methyl and ethyl groups in the *meso* positions of thia-, oxa- and selenacarbocyanines.[2,77,78] Taking into account considerable differences in the tendency of structurally similar dyes to form J-aggregates, small modifications would be expected to change the mutual orientation of the molecules responsible for their interactions. The specificity of the influence of an increase in the bulkiness of substituents was observed even in a single series of dyes. For example, the ability of 9-ethyl-6,6′-dimethoxycarbocyanines to form J-states is substantially higher than that of the corresponding 6,6′-diethoxy and, particularly, 6,6′-dipropoxy derivatives, whereas the tendency to form H-states substantially increases in this series.[77]

It is commonly accepted that the ability to form aggregates is enhanced in the presence of halogen (except for iodine) atoms and COOR, CN and some other electron-withdrawing groups in the heterocyclic rings of indo-, imida, quino(2,2′)- and oxacarbocyanines containing unsubstituted chains due to a strengthening of $\pi-\pi$-electron interactions between the molecules.[87] The influence of other substituents is very specific.

In the quino-(2,2′)-cyanine series, *N*,*N*′-dimethoxides are much less prone to J-aggregation than ethoxides.[78] Sheppard *et al.*[88] demonstrated that this property is inherent also in methoxides of cyanines prepared from other bases, in particular, from benzothiazole and benzoxazole. *N*,*N*′-Dimethoxides of quino-, oxa-, thia- and selenacarbocyanines are less efficient due to their high ability to form photochemically inactive H-polymers.[77] If methoxides and ethoxides of thia-, imida- and indocarbocyanines are characterised by a similar tendency to undergo polymerisation, they are similar in the sensitising action. The intensity of the J-band sharply decreases with increasing number of carbon atoms in the alkyl groups at the nitrogen atoms ($C_2H_5-n\text{-}C_4H_9$) in the series of 5,5′-disubstituted 9-ethylthiacarbocyanines,[78] whereas the intensity of this band remains virtually unchanged in the case of imidacarbocyanines.[77] In the series of dimethinemerocyanines, *viz.*, rhodanine and thiohydantoin derivatives,[78] the ability to form J-aggregates, on the contrary, either appears or is enhanced.

Among carbocyanines containing alkyl and sulfoalkyl substituents, dyes containing sulfoalkyl groups at the nitrogen atoms are more prone to aggregation, the photographic activity of J-states being much higher than that of dyes containing alkyl substituents with different structures.[3]

As mentioned above, the ability of dyes to form various polymolecular states is enhanced in the presence of methyl and ethyl groups at the *meso* position of the polymethine chain of thia-, oxa- and selenacarbocyanines. A comparison of the sensitisation and absorption spectra of dyes and the experimental relative quantum yields of sensitisation for several groups of dyes demonstrated that the introduction of methyl and ethyl groups at the *meso* position of carbocyanines leads to the formation of the photochemically active H_1- and J_1-states of 9-methylcarbocyanine and the J_2- or J_3-states of 5,5′-disubstituted 9-ethylthiacarbocyanines in the adsorption layer.[77,78] More recently, it was found that the common polymolecular herringbone structure characterised by two spectral transitions rather than two different states (H_1 and J_1) are formed for 9-methyl-substituted thiacarbocyanines.[80,89] In these studies, as well as in other investigations (see references in the publication[20]), the introduction of alkyl groups at the *meso* position was demonstrated to have a substantial effect on the enhancement of J-aggregation, the replacement by the ethyl group being more favourable for the *cis* configuration, whereas the presence of structurally identical dye molecules facilitates their self-assembly as J-aggregates.

The dependence of the ability to form aggregates not only on the number of isomers, but also on such factors as the planarity of cyanine molecules and the absence of internal rotational motion was examined[84,86,90] and the contribution of these factors to the colour and the ability to undergo polymerisation and be sensitised was investigated. The compactness of molecules and a small deviation from planarity are particularly favourable for aggregation because planar molecules more readily form close-packed relatively rigid structures, which are less susceptible to thermal decomposition. Brooker *et al.*[86] classified dyes into free, compact and overcrowded. The first two groups involve planar molecules and the third group includes nonplanar molecules. The fact that substituents violating the planarity of molecules hinder aggregation is well illustrated by 1,1′-diethyl-2,2′-cyanine derivatives. The tendency of this compact dye to form aggregates is weakened by 3,3′-alkyl substituents, which push the heterocyclic rings out of the plane of the molecule. In some cases, the required compactness and the related ability to form aggregates can be achieved by fixing the heterocyclic moieties by bridging groups, thus forming a rigid cyclic structure of the molecule. This is typical of *N*,*N*′-ethylenebenzimidazolocyanine, which readily forms J-aggregates on the surface of AgHal. By contrast, the sterically hindered and nonplanar *N*,*N*′-diethyl-substituted analogue cannot undergo aggregation.[17,91]

Carbocyanine derivatives of *N*,*N*′-dialkylbenzimidazoles were studied in detail.[77,78] The introduction of alkyl substituents at position 9 of these dyes causes a substantial deviation from coplanarity and decreases the ability to form J-aggregates. Likewise, the introduction of bulky substituents, such as NO_2, SO_2CF_3 or SCF_3, at position 5 of the heterocycle suppresses the formation of J-aggregates of compact *N*,*N*′-dialkylbenzimidazole molecules on the surface of AgHal.

The introduction of the CH_3O and C_6H_5 groups at the *meso* position of the chain and of aryloxy groups at positions 8 and 10 can assist aggregation of oxa- or thiacarbocyanines, which are aggregated poorly, if at all, because it becomes possible to form compact structures from all-*trans* or mono-*cis* configurations.[25,26] Taking into account the role of substituents in the chain and at the nitrogen atoms of the ring, it was hypothesised that small deviations from the plane of the dye molecule due to the presence of ethyl and other groups, can facilitate the formation of J-states with a brickwork structure from compact planar dye molecules.[92,93]

Therefore, the factors favourable for the planarity of a molecule, an elongation of the π-conjugated system of the dye and the uniformity of the isomeric composition of the molecule are responsible for the ability to form J-aggregates. However, these are necessary but not sufficient conditions for J-aggregation. Since J-aggregates are particular three-dimensional packings of dye molecules, J-aggregation depends on the volume of the substituents both in the rings and the chain, which can cause steric hindrance to interactions of the π-conjugated systems of dyes in aggregates.

2. Influence of emulsion factors on aggregation of spectral sensitisers

The nature of the halogen atoms in AgHal microcrystals of photographic emulsions is one of the most important factors influencing J-aggregation. It is known[2,3] that the adsorption strength of cyanine dyes on AgHal powders decreases in the series AgI > AgBr > AgCl. For many dyes, J- and H-aggregation decreases in the following series: AgBr(I) > AgBr > AgBr(Cl) > AgCl.[77,78] Meyer[94] was the first to find that the introduction of 3 mol.% of silver iodide into crystals of a silver bromide emulsion substantially enhances J-aggregation of 9-ethyl-3,3′,5,5′-tetramethylthiacarbocyanines accompanied by an increase in the light sensitivity of photolayers.

The influence of the nature of halide ions in monodisperse emulsions containing cubic and octahedral crystals was investigated[95] and J-aggregation of microcrystals of the same habit of silver chloride bromide and silver bromide iodide emulsions was demonstrated to be better compared to silver chloride emulsions.

Aggregation of dyes upon adsorption on AgHal microcrystals of different habits was studied in depth.[77,95–106] It was noted[100,101] that absorption spectra of some dyes in emulsions prepared by the ammonia method differ from those prepared by the ammonia-free method. In neutral emulsions, the conditions

for aggregation of dyes are more favourable than those in ammonia emulsions. This may be associated not with the presence or absence of ammonia in the emulsion but with the different habits of microcrystals (a spherical habit in ammonia emulsions and a tabular habit in neutral emulsions).

Dye aggregation on cubic and octahedral AgHal microcrystals has been studied in sufficient detail. It was found that aggregation of cyanines on the (100) faces differs from that on the (111) faces. Experimental data and a theoretical justification for the predominant J-aggregation on the surface of octahedral crystals were reported.[95–99, 102, 105] 9-Methylthiacarbocyanines, which form J_2-aggregates on the (111) faces giving a band at $\lambda_{max} = 625$ nm and aggregates on the (100) faces characterised by two absorption bands at $\lambda_{max} = 590$ and 520 nm, were primarily used as model compounds.

It was found [97, 102] that readily aggregating dyes (imida- and 5,5′-dichloro-9-ethylcarbocyanines) form, at low concentrations, J-aggregates predominantly on octahedra. Adsorption of cyanines is determined by Coulombic interactions between the negatively charged (111) surface and the positively charged terminal nitrogen atoms of a polymethine chromophore. The fact that the distances between the molecules in the aggregate are similar to those between the ions on the surface of octahedral AgBr microcrystals satisfies the requirement for a closer packing, which is also favourable for J-aggregation. In spite of steric and electrostatic hindrance, readily aggregating dyes whose aggregation is facilitated by water molecules are primarily adsorbed in the J-state on the (100) faces. Tani [102] found that not only J-aggregation but also H-aggregation of cyanines is stronger on the (111) faces than on the (100) faces.

It was noted [99] that J-aggregation of dyes, in particular, of 9-methylthiacarbocyanines, occurs predominantly on the (100) faces of AgCl analogous to that observed on the (111) faces of AgBr. It was hypothesised that J-aggregates are additionally stabilised by denser solvate shells. This is due to the difference in the influence of Cl^- and Br^- ions on the structure of water on the surface. In the presence of chloride ions, the solvation effect is enhanced,[96] and, consequently, hydrophobic binding of dye molecules with each other is possible.

On the contrary, experimental data on the enhancement of J-aggregation of dyes on cubic microcrystals were reported.[103–107] A small amount of a dye is sufficient for J-aggregation because the (100) faces contain a small number of crystal lattice defects.[104] Octahedral microcrystals contain a larger number of surface defects. Hence, H-aggregation occurs at low concentrations, whereas higher concentrations of dyes are necessary for J-aggregation. Kazmierczak and Markocki [106] studied the photographic action of thia-, oxa- and selenacarbocyanines at different pAg and pH of emulsions. It was found that particular elements of the dye molecules can facilitate J-aggregation on either (100) or (111) faces. Carbocyanines containing methoxy or phenyl groups at position 5 of heterocyclic fragments show a tendency to form J-aggregates on the (100) faces. Unsubstituted dyes are more prone to J-aggregation on the (111) faces. 5,5′-Dichloro- or 5,5′-dimethyl-substituted carbocyanines behave analogously. Some dyes form J- or H-aggregates regardless of the habit of AgHal microcrystals.

Grishina [108] found that the influence of different structural elements of anionic and cationic thiacarbocyanines on J-aggregation has a general character and is independent of the habit and homogeneity of AgHal microcrystals. More stable J-aggregates are formed on the (100) faces compared to those on the (111) faces.

The size of emulsion microcrystals is yet another important factor determining J-aggregation of spectral sensitisers. However, the available published data do not allow one to reveal general features of dye aggregation depending on the dispersion of silver halide microcrystals in photographic emulsions.

Of all sensitisation bands, the J-band is most dependent on the additives. The concentration of Ag^+ ions in emulsions and pH of the medium have a considerable effect on J-aggregation. In an aqueous medium under ambient conditions, the surface of AgBr is stoichiometric to the lattice ions at pAg 5.3. The surface of AgBr acquires a negative charge as the concentration of Br^- ions increases. The limiting surface area, which can be occupied by adsorbed bromide ions, is ~20% of the surface area of the microcrystals, a particular concentration of Br^- ions corresponding to each habit.[3] Adsorption of dyes leads to a shift of the equilibrium between the bromide ions in solution and on the surface and an increase in pAg. The amount of the adsorbed dye and the strength of adsorption on the surface of AgBr depend on the structure of the dye. For example, merocyanines and cationic dyes, which bind silver ions, are adsorbed in larger amounts at lower pAg. Adsorption of cyanines binding bromide ions is favoured by an increase in pAg.[3] However, it was demonstrated [99] that adsorption of certain cationic carbocyanines depends only slightly on the change in pAg in a rather wide range and substantially decreases only at rather high silver ion concentrations (pAg < 4).

The influence of pAg on adsorption of cyanines having different structures is often determined by the influence of this factor on J-aggregation in the adsorption layer. An enhancement of the tendency to form J-aggregates upon adsorption of dyes on an AgBr powder from ethanol was observed in the presence of an excess of both Br^- and Ag^+ ions.[109, 110]

In investigations of spectral sensitisation of photographic emulsions,[5, 110] the degree of dye aggregation not necessarily changes with decreasing concentration of bromide ions (during washing of sensitised layers with water with the aim of increasing the light sensitivity). More recent studies demonstrated [111] that J-aggregation of many cyanines is suppressed in the presence of an excess of silver ions, a considerable amount of dyes being displaced to gelatine. The addition of an $AgNO_3$ solution (to pAg 3–4) to a monodisperse emulsion before the addition of a spectral sensitiser led to suppression of J-aggregation of quino-2-cyanines compared to J-aggregation in the starting emulsion. This was not observed in the case of other mono- and trimethinecyanines.[112] Therefore, J-aggregation of cyanine dyes depends not only on pAg but also on the way of changing this parameter.

Cyanine dyes are bases whose protonation constants differ by 14 orders of magnitude [17] depending on the structure of the dye and, as a consequence, the influence of pH on aggregation is substantially different for dyes having different structures. Generally, an increase in pH leads to a particularly substantial weakening of the J-band of basic cyanines as pH is lowered. The following factors cause a decrease in the effect of pH on J-aggregation: the cubic habit of microcrystals, high concentrations of I^- ions in the substrate, an excess of Hal^- ions in the solution, a high molar absorption coefficient of the dye and the absence of competitive adsorbents.[113, 114] It should be taken into account that pAg and pH can substantially depend on the presence of sensitisers and other additives in emulsions. For example, the addition of a sensitiser to an acidic emulsion followed by an increase in pH does not lead to a weakening of J-bands of thiacarbocyanines.

For dye aggregation, not only pAg, pH and the nature of the adsorbent but also the nature of gelatine, which is used in photographic emulsions as a dispersion medium, are of considerable importance. The influence of gelatine was examined in a number of studies (see, for example, Ref. 20). The absorption spectra of dyes substantially depend on the gelatine concentration. Small amounts of gelatine serve as aggregation sites, while the carboxy groups of gelatine can serve as adsorption sites for dyes in solution. The influence of gelatine on J-aggregation, in particular, the dependence of J-aggregation on the concentration of gelatine and its type, was studied.[20] Dye aggregation starts on particular sites of gelatine molecules. The concentrations of these sites in different types of gelatines are different.

The influence of gelatine on J-aggregation of cyanine dyes is associated with pH,[20] because gelatine is a polyelectrolyte, different types of gelatine having somewhat different isoelectric points.

The influence of the main stabiliser of photographic emulsions of 4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene (sta-salt) on aggregation of different dyes was studied in detail by Shapiro *et al.*[79,80,115–118] The action of the sta-salt on quino-2,2′-cyanine was examined. In the study of an emulsion containing cubic AgBr microcrystals with dimensions 0.17 μm subjected to gold and sulfur sensitisation, the sta-salt was demonstrated to cause a transformation of the J-band (λ_{max} = 575 nm). At low concentrations of the sta-salt, this band is shifted to shorter wavelengths; an increase in the concentration of the sta-salt to $(2-5)\times10^{-3}$ mol per mole of AgBr gives rise to two distinct absorption bands at λ_{max_1} = 570 nm and λ_{max_2} = 580 nm; at the sta-salt concentration of $\geqslant(8-10)\times10^{-3}$ mol per mole of AgBr, one J_2-band appears at longer wavelengths. However, the character of aggregation and the efficiency of supersensitisation substantially depend on the order of addition of the sta-salt and a dye. The action of the sta-salt was related[115–118] to adsorption on surface defects, on which J-aggregation starts. Aggregation is suppressed by stabilisers belonging to heterocyclic thio derivatives (benzothiazole-2-thiol and 1-phenyltetrazole-5-thiol).[119]

The addition of various surfactants to emulsions causes changes in the absorption spectra of J-aggregating sensitisers.[120,121] It was concluded that J-aggregates of anionic cyanine dyes are more stable against surfactants, which are used as precipitants of the solid phase, than those of cationic dyes.

The addition of colour-forming non-diffusing components (CNC) to an emulsion medium impairs J-aggregation of cationic cyanine dyes.[77,78] This is attributed to desorption of the sensitiser from the surface of emulsion microcrystals. J-Aggregates of betaine dyes are even more stable against the desorption action of CNC; for these dyes, spectral sensitisation in the J-band is retained in the presence of CNC.[77] This fact was also noted by Lifshits and co-workers (see references in the publications[77,78]), who demonstrated the stability of cyanine dyes against CNC to increase upon fusion of benzene and thiophene rings. The sensitising action of J-bands of benzimidacarbocyanines in the presence of CNC is enhanced by the Hal, CF_3, CN and CO_2R substituents in heterocyclic fragments. This may be associated with an increase in the strength of bonds in J-aggregates on AgHal microcrystals.

Bis-quaternary salts, in particular, benzimidazole derivatives,[122–124] contrary to CNC, facilitate J-aggregation. In the presence of bis-quaternary salts, the J-band is shifted to longer wavelengths and its intensity slightly increases. Such changes were observed, for example, in the spectra of 3,3′-di(γ-sulfopropyl)-9-ethyl-4,5,4′,5′-dibenzothiacarbocyanine betaine. An increase in the intensity of J-bands, including the appearance of J_2- and J_3-bands, was observed also for other carbocyanines, which show a weak tendency to form long-wavelength aggregates characterised by the highest photographic efficiency. According to the results of the study,[124] co-adsorption of dyes and bis-quaternary salts results in an increase in the strength of adsorption of polymethine dyes against the desorption action of CNC. The influence of bis-quaternary salts of α-picoline on J-aggregation of cyanine dyes was examined.[125,126] The addition of a bis-quaternary salt of α-picoline at concentrations similar to the concentrations of the dye was demonstrated to enhance J-aggregation. This phenomenon is arbitrarily called catalysis of aggregation.

J-Aggregation is enhanced in the presence of inorganic I^-, CN^- and SCN^- anions.[2,77,78] These cations form poorly soluble salts with Ag^+ ions and, being located in the adsorption layer, provide prerequisites for a close packing of dyes, resulting in a substantial increase in aggregation adsorption. The influence of these anions on J-aggregation and photographic efficiency of thiamonomethinecyanines adsorbed on cubic AgCl microcrystals and planar AgBr(I) microcrystals was examined.[127] It was found that J-aggregates of thiamonomethinecyanines are formed in the presence of the I^-, CN^- or SCN^- ions and the efficiency of spectral sensitisation substantially increases. The most pronounced effect was observed in the presence of SCN^-.

In the presence of SCN^-, adsorption is increased and J-aggregation of thiamonomethinecyanines and oxa-, imida- and thiacarbocyanines on cubic AgCl microcrystals is enhanced.[128–131] The factors responsible for the observed changes were revealed.[128] Electronic photographs of microcrystals of the starting emulsion and the emulsion treated with a KSCN solution were published. Surface etching occurs on microcrystals treated with rhodanide ions, and pronounced outgrowths are observed at the vertices and edges of AgCl cubes. An increase in the structure imperfection due to formation of a new phase (apparently, of AgSCN) is favourable for nucleation and growth of J-aggregates. This is accompanied by a substantial increase in the spectral sensitivity at the maximum of the J-band. The introduction of SCN^- ions into an AgCl emulsion before the addition of a dye solution[83] is favourable also for J-aggregation of thiadicarbocyanine dyes, which serve as spectral sensitisers for the IR spectral region, thus substantially shifting the spectral sensitivity range to the IR region.

J-Aggregates consisting of two different dyes are of particular interest. It should be noted that data on such J-aggregates are scarce. The formation of mixed J-aggregates from two thiacarbocyanine dyes having different structures was documented.[132] Absorption spectra of photographic layers sensitised by individual thiacarbocyanines and their composites are shown in Fig. 16 *a*. Each dye forms its own J-aggregate. The simultaneous

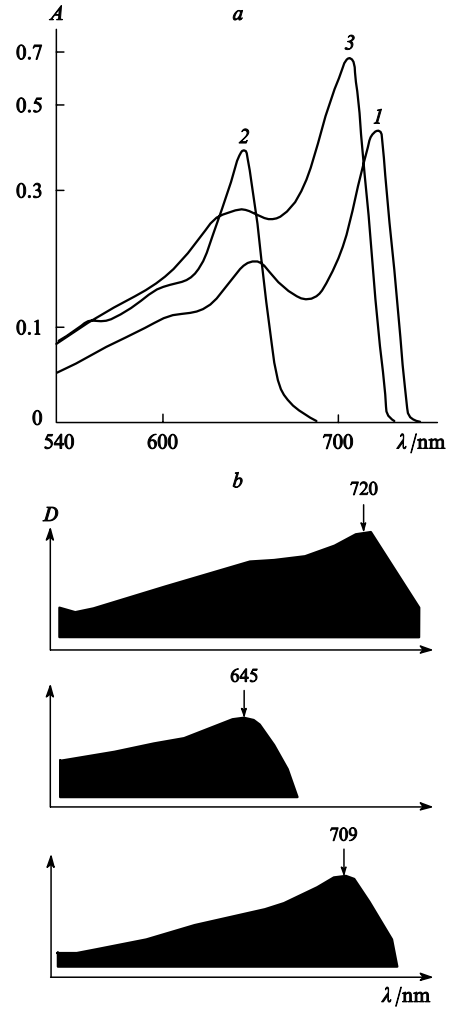


Figure 16. Absorption spectra of photographic layers sensitised by 3,3′-diethyl-5,5′-dimethoxy-8,10-dimethylenethiacarbocyanine tosylate (*1*), the pyridinium salt of 3,3′-di(γ-sulfopropyl)-5,5′-dimethoxy-9-ethylthiacarbocyanine (*2*) and their composite (*3*) (*a*) and the spectrograms of the corresponding layers (*b*);[132]
D is the blackening density.

addition of equimolar concentrations of dyes to an emulsion gives rise to a new J-band (curve *3* in Fig. 16 *a*), the intensities of the J-bands of individual dyes being decreased. The spectrograms obtained on the corresponding photographic layers (Fig. 16 *b*) are clear evidence of the formation of a new photochemically active J-band, whose maximum is between the sensitisation maxima of the individual J-bands of two dyes. The principal conclusion [132] was that the position of the sensitisation maximum can be varied over a wide range by changing the concentrations of dyes involved in mixed J-aggregates.

Mixed J-aggregates of thiacarbo- and thiadicarbocyanines were examined in the study.[133] The results are presented in Fig. 17. The method of formation of mixed J-aggregates allows the selection of J-aggregates. In this case, a new J-aggregate inherits the properties of the parent dyes. For example, mixed J-aggregates containing carbo- and dicarbocyanines combine the efficiency of carbocyanines with the spectral sensitisation zone in the IR spectral region characteristic of dicarbocyanines.[134] The formation of mixed J-aggregates from oxacarbocyanines having different structures was observed for the first time in the study.[135] The problem of supersensitisation in mixed J-aggregates of thiacarbocyanine dyes was discussed.[136]

In the studies,[137, 138] the possibility of the formation of mixed and heterocontact J-aggregates from thiacarbocyanine and monomethinecyanine dyes both in an aqueous gelatine solution and on the surface of AgBr(I) crystals with (S + Au)-chemical sensitisation was examined. The structures and properties of mixed J-aggregates formed on the surface of AgHal were studied.[139]

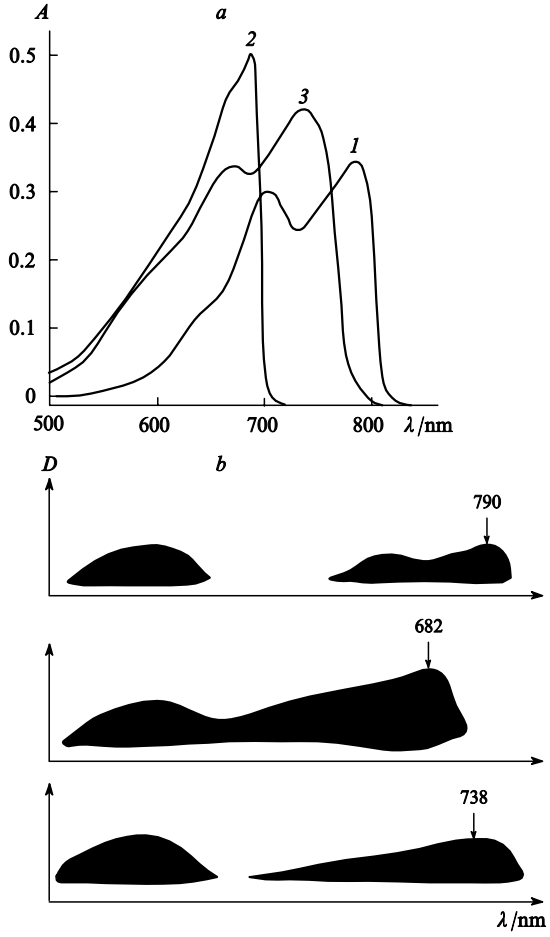


Figure 17. Absorption spectra of photographic layers sensitised by the triethylammonium salt of 5,5′-dichloro-3,3′-di(γ-sulfopropyl)-9,11-(β,β-dimethyltrimethylene)-10-methylthiadicarbocyanine (*1*), the pyridinium salt of 3,3′-di(γ-sulfopropyl)-4,5,4′,5′-dibenzo-9-ethylthiacarbocyanine (*2*) and their composite (*3*) (*a*) and the spectrograms of the corresponding layers.[133]

From the aforesaid, the following conclusion can be drawn. Since J-aggregation of dyes occurs on the surface of AgHal microcrystals, the J-aggregation process often more substantially depends on the surface state than on changes in the structure of the dye. The surface state of microcrystals in an emulsion is determined primarily by their habit. It is known [111] that the (111) surface has a larger number of jogs and kink-sites, *i.e.*, it is more imperfect than the (100) surface. Hence, the (111) surface contains a larger number of sites with an excessive energy at which nucleation of J-aggregates can occur. Therefore, the nucleation of aggregates should occur more easily on the (111) surface. However, J-aggregation, like crystallisation, includes two steps, *viz.*, nucleation and crystal growth (growth of J-aggregates). Presumably, the subsequent growth of J-aggregates, which determines the position of the absorption maximum of the J-band, occurs more readily on the less imperfect (100) surface on which the smaller number of J-aggregates are nucleated. It is the contribution of these two steps that determines J-aggregation of a particular dye. If a dye is not prone to J-aggregation, nucleation more readily occurs on the (111) surface. However, an increase in the size of aggregates on this surface is unlikely. On the contrary, if a dye is prone to aggregation, nucleation does not limit the process and ordered J-structures more readily grow on the (100) surface of the crystal. Apparently, the different contributions of these processes to the formation of J-aggregates account for the seemingly contradictory published data on the ease of aggregation on the (111) and (100) surfaces.

Evidently, the charge state of the surface of AgHal microcrystals is determined by the concentrations of the Ag^+ and Hal^- ions in an emulsion. In the presence of an excess of Ag^+, adsorption of molecules of certain dyes (particularly those containing sulfur atoms) on the surface is facilitated, which hinders J-aggregation. Compounds adsorbed on the surface of AgHal (surfactants, thio derivatives and various heterocyclic bases), particularly those which are capable of forming poorly soluble complexes and salts with silver ions, should play a great role. Apparently, stabilising and antifoging compounds and inorganic ions belong to this class.

Therefore, J-aggregation is determined not only by the molecular structure of dyes but also by parameters combined under the general name 'emulsion factors'.

3. Structures of dye aggregates adsorbed on AgHal microcrystals

The aggregate structures both in solution [140] and in crystals [15] were studied in depth. It was noted that J-aggregation in solution is similar to crystallisation. In particular, two steps are distinguished: nucleation and aggregate growth.[141]

As mentioned above, dye molecules differ in the ability to form aggregates depending on their structure. In the general case, J-aggregation more readily occurs on the surface of solid phases than in solution. The numbers of monomeric fragments involved in J-aggregates of dyes in aqueous solutions were determined by different methods.[3, 16–18, 20, 142] The degree of polymerisation of aggregates can vary from 2 to 10^6 depending on the molecular structure of the dye and the method used for the determination. The main methods for the determination of the number of molecules in J-aggregates in solution were described in the publications.[3, 16, 24]

In early studies, a knowledge of the structures of J-aggregates was based on X-ray diffraction data obtained by Hoppe [143] for aggregates of 2,2′-cyanine dyes. These results are as follows:

— individual dye molecules are extended parallel to each other;

— short axes of dye molecules are inclined to the axis of the aggregate; the deviation from the normal is 35°;

— the normal distance between the molecules along the axis of the aggregate is ~3.6 Å.

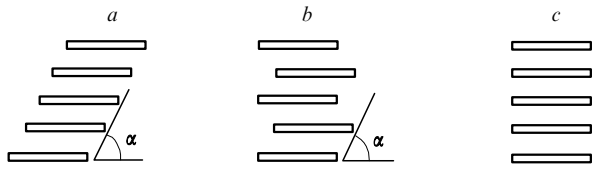


Figure 18. Models of structures of J- (*a*, *b*) and H-aggregates (*c*) of cyanine dyes.[144, 145]
A slipped-deck-of-cards structure: a staircase structure (*a*) and a ladder structure (*b*).

In early studies, Scheibe *et al.*[144, 145] proposed models for structures of J-aggregates as a slipped deck of cards, *viz.*, a staircase and a ladder, with consideration for the results obtained by Hoppe (Fig. 18 *a*,*b*). The authors reached a conclusion that dye cations are adsorbed on edges of AgHal in close-packed monolayers. Based on the degree of light polarisation in absorption bands of quino-2,2′-monomethinecyanine aggregates on freshly cleaved mica crystals, the angle α between the plane of the molecules and the axis of the aggregate was estimated as $\sim 55^\circ$. At the same time, the plane of the molecule in the structure of H-aggregates (a hypsochromic shift) is perpendicular (in the authors' opinion) to the axis of the aggregate (Fig. 18 *c*).

The above-considered structures of J-aggregates were generally accepted until the late 1960s. Bird and co-workers [33] refined the basic staircase structure proposed by Scheibe with the use of the point-dipole theory. These results contribute to the development of an idea, according to which the main structures of H- and J-aggregates are, in principle, identical. However, $\alpha < 54^\circ 44'$ in J-aggregates and $\alpha > 54^\circ 44'$ in H-aggregates. The initial version of the point-dipole theory was inapplicable to precise quantitative calculations of J-aggregates. Hence, this theory was improved based on the quantum-chemical model of interactions between molecules in aggregates taking into account electron cloud overlap (an electron gas model). This theory was applied to large aggregates of various dyes, and, although the results of calculations were inaccurate, they allowed one to obtain correct orders of the angles.

Presumably, aggregates of cyanine dyes in solution differ from those adsorbed on a substrate in that the structure of adsorbed aggregated is related to the crystal lattice structure of the adsorbent and molecules in adsorbed aggregates are packed less closely than in solution. This is evidenced by the results of spectroscopic studies. J-Aggregates of the same dye give a narrower J-band in solution compared to that in the adsorbed state. Apparently, this is associated with the affinity of particular fragments of cyanine dye molecules for local regions of the surface of AgHal.[93]

Bird and co-workers [146–148] applied an improved point-dipole model to a specific case of benzothiazole dyes on an AgBr substrate. Circular dichroism measurements of adsorbed J-aggregates demonstrated that dye molecules are oriented in a particular fashion on different faces of AgBr microcrystals.[147] It was postulated [146, 147] that the long axis of the dye molecules in aggregates is oriented predominantly on the surface of microcrystals along the [110] direction. In this case, rows of Ag^+ ions on the surface of a cube are at a distance of 4.08 Å, whereas rows on the surface of an octahedron are at a distance of 3.54 Å, *i.e.*, at a distance similar to the standard intermolecular distance in the graphite lattice (3.4 Å) found [20] for the packing of planar aromatic molecules. Bird suggested that chemisorption of dyes is accompanied by the formation of bonds between the Ag^+ ions of the AgBr lattice and the sulfur atoms of the benzothiazole moieties of the molecules, which form a structure of a slipped-deck-of-cards type and are adsorbed so that the sulfur atoms are oriented toward the surface of microcrystals and the NR groups border the solution. As a consequence, the formation of particular aggregate structures of dye molecules with a lateral shift by 3, 2, 1 or 0 ionic radii can be formed on the octahedral surface. An application of this chemisorption model to cubic microcrystals presents certain difficulties.

The slip angles of dye molecules along the aggregate axis (α) in the structures formed on the octahedral surface are 19, 30, 60 and 90°. According to Bird's theory, the slip angles of 90 and 60° corresponding to Scheibe's staircase structures are assigned to H-aggregates; the slip angles of 30 and 19°, to J-aggregates. These angles are well consistent with the spectral shifts of absorption bands of aggregates.[20] The results of calculations performed within the framework of the molecular-exciton theory [149] confirmed the aggregate structures for thiacarbocyanine and its homologue. The largest bathochromic shift for linear J-aggregates corresponds to the angle of 19° between the long molecular axis of the dye and the axis of a J-aggregate.

The same slip angles (90, 60, 30 and 19°) were expected along the [110] direction on the (111) surface of AgCl. However, in this case the dye molecules should be located closer to each other than along the [110] direction on the octahedral surface of AgBr, because the rows of ions along the [110] direction on AgCl are located at a distance of 3.4 Å.

The researchers encountered obstacles when generalising Bird's model to the (100) surface of cubic AgBr, because the distance between the rows of silver ions along the [110] direction is larger (4.08 Å) than the graphite-like distance for aromatic structures. Bird proposed a model,[150] in which the assumed $Ag^+ \cdots S$ bond is deformed and, hence, the angle between the long axis of the dye molecules and the [110] direction is 24.4°. Smith demonstrated [151] that a rotation of the molecule by only 5° is necessary for the aggregate structure to be identical to that present on the (111) surface; however, the angle α is equal to 21.7°.

A study of the aggregate structures of some sensitising dyes adsorbed on AgI, AgBr or AgCl by electron diffraction demonstrated [20] that the 1,1′-diethyl-2,2′-cyanine and 3,3′,9-trimethylthiacarbocyanine molecules are inclined to the surface of AgHal, and the inclination angle depends on the nature of Hal^-. It was concluded [20] that the molecules are arranged in a regular fashion corresponding to strong adsorption forces. If adsorption forces are weak, the aggregate structure is disordered.

Based on the data on aggregation of thia- and oxacarbocyanines and taking into account the steric factors, it was concluded [20, 152, 153] that the formation of the epitaxial $Ag^+ \cdots S$ bond proposed by Bird is highly improbable and this bond is of secondary importance in adsorption. The sizes of dye molecules do not necessarily correspond to the crystal lattice parameters of silver halide. The distances between the rows of molecules and the slip angles in the aggregates are determined by the molecular geometry and intermolecular interaction forces rather than by chemisorption forces, which, in turn, depend on the structure of dyes (the nature of heterocycles and substituents both in the chain and heterocycles and the length of the polymethine chain).

A model of physical adsorption of dyes on the surface of silver halide was proposed.[154] The adsorption is considered as a function of the crystallographic lattice parameters of AgHal. In the studies,[147, 154] the adsorption of dyes was considered taking into account that the ideal (111) and (100) surfaces do not exist because of Coulombic restrictions. It is known that such surfaces contain a large number of steps parallel to the [110] direction. The orientation of the molecules of aggregated cyanine dyes formed upon adsorption is determined by the presence of steps on the surface of AgBr microcrystals. The rate of J-aggregation of pseudocyanine was higher on a larger number of defect sites of the (111) surface. The average size of J-aggregates is smaller and absorption occurs at shorter wavelengths compared to those on the (100) surface and other surfaces. The dichroism was studied as a function of the deviation of the growth direction of a dye aggregate *vs.* the [110] direction and as a function of the deviation of the real crystal surface from the perfect surface. The orientation of J-aggregates of pseudocyanine along the [110] direction was preferable. However, this tendency was not revealed for other eleven known thia-,

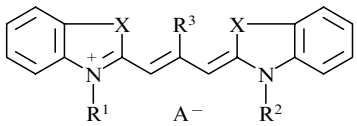
oxa- and imidacarbocyanines. Presumably, a complex variation of the arrangement of the dye molecules on the surface steps with different *hkl* indices *vs.* the dye structure and the absence of a pronounced orientation along the [110] direction are evidence that chemisorption plays an insignificant role.

Maskasky [155] also cast doubt on the occurrence of chemisorption in the case of aggregation of oxa- and imidacarbocyanines on cubic and planar AgCl and AgBr microcrystals. The orientation of J-aggregates on AgCl along the [110] and [100] directions studied by low-temperature luminescence microscopy remained unexplained within the framework of the theory of chemisorption. It was hypothesised that J-aggregates are located along surface defects of microcrystals (surface steps).

It was established that chemical bonding and Coulombic attraction make a particular contribution to aggregation of most dyes. However, van der Waals forces between a polarisable substrate and delocalised π-electrons of dyes contribute the most to adsorption.[3] This accounts for the fact that the heats of adsorption of cyanines on more polarisable AgBr and AgI are higher than that on AgCl.[156, 157] However, the model of chemisorption appeared to be useful in considering certain problems of spectral sensitisation, such as the dependence of absorption spectra of adsorbed dyes on the habit and halide composition of microcrystals,[98, 147, 148, 158] the mechanism of supersensitisation,[6] the influence of substituents in the chromophore chain on the spectral shifts and the relationship between the structure of aggregates and their adsorption.[90, 146–148, 159–161]

Taking into account the model of chemisorption, Reich [27] explained the observed two-band spectrum in the case of adsorption of 3,3′-bis(β-carboxyethyl)-5,5′-dichlorothiacarbocyanine on AgBr and AgCl microcrystals. He proposed a model of J-aggregates consisting of two non-parallel stacks of dye molecules, in which one stack is adsorbed along the [110] direction of AgHal microcrystals, whereas another stack is adsorbed along the [101] direction to form a herringbone structure (see Fig. 5 *b*). The results of calculations of the energy splitting in electronic spectra of aggregates are consistent with the experimental data for a herringbone structure with $\alpha = 30^\circ$ within each stack for an octahedral surface and with $\alpha = 35^\circ 5'$ for a cubic surface (the spectra contain broad bands in the visible spectral region).

Adsorption isotherms were used in early studies of aggregation. However, it is known that these isotherms do not allow one to establish unambiguously whether dyes are adsorbed as individual molecules or aggregates. This problem can be solved only by comparing adsorption isotherms and reflection spectra.[3, 20, 159] The initial weak rise of adsorption isotherms up to an inflection point for carbocyanines of the type



X = S, Se, NR, CH=CH, O; A^- — counterion;
R^1–R^3 — substituents.

is accounted for by the fact that the molecules are initially adsorbed on the microcrystal surface by their planes. Further adsorption results in that the dye molecules take edgewise orientation and form a monomolecular layer of a close-packed aggregate, which is accompanied by the appearance of an inflection point in the isotherm.[103] Another explanation is that the dye molecules are adsorbed on the long edge of the molecule perpendicular to the microcrystal surface even at low concentrations, but the molecules are disordered. An increase in the dye concentration gives rise to larger ordered aggregates.

Based on the results of investigation of the shifts of spectral absorption bands and their comparison with the shifts calculated by a quantum chemical method, Kuhn and co-workers [22, 162, 163] proposed a generalised two-dimensional model of a brickwork arrangement of dye monomers (see Fig. 5 *a*). In the case of a two-dimensional aggregate structure and the appropriate angle α, one type of aggregates can be transformed into another type (H-aggregates are transformed into J-aggregates with decreasing α and *vice versa*). A quantitative examination of X-ray spectra [164] of *meso*-alkyl-substituted thiacarbocyanines revealed the existence of J-aggregates formed in a brickwork fashion from sandwich dimers, which consist of monomers with the oppositely directed *meso*-alkyl groups.

It is rather difficult to determine the degree of polymerisation in the case of formation of adsorbed J-aggregates. It is hardly correct to extrapolate large self-association numbers for dyes in solution (an order of 10^2) to adsorbed J-aggregates, because the properties of aggregates depend only slightly on the number of molecules in the aggregates if the self-association number is rather large. A reasonable conclusion is that the number of molecules in aggregates is small and the lower limit for the size of J-aggregates corresponds to the ratio of the sensitiser concentration to the supersensitiser concentration in mixed aggregates, at which the J-band of a supersensitiser disappears. According to estimates, J-aggregates of a pseudocyanine should contain at least three molecules. It is known that adsorbed dyes form several aggregates, which substantially differ in absorption and position of the energy levels.[115–118]

Tani *et al.*[165–168] made an attempt to determine the number of molecules in J-aggregates of *meso*-ethyl-substituted thiacarbocyanine by a spectroscopic method from the ratio of the half-widths of absorption bands of the monomer to those of an adsorbed J-aggregate of the dye. The calculated numbers of the molecules vary from 5 to 15. Studies by the desorption method demonstrated [169] that J-aggregates of thiacarbocyanine on the (111) surface included 10–37 molecules; on the (100) surface, 34–53 molecules.

In the studies,[129–131] the sizes of J-aggregates of thiamonomethinecyanines [129] and oxa-, imida- (see Ref. 130) and thiacarbocyanines [131] in an AgCl emulsion containing cubic microcrystals were estimated from the ratio of the half-widths of absorption bands of the monomers to those of adsorbed J-aggregates of the dyes. The calculated numbers of the molecules were 2–7, 3–4, 6–27 and 6–12 for thiacyanines, oxacarbocyanines, imidacarbocyanines and thiacarbocyanines, respectively.

Recently, due to an improvement of experimental technique, it has become possible to study the sizes of J-aggregates by direct observation using atomic force microscopy (AFM). It was found [170] that molecules of triethylammonium salt of 3,3′-di(γ-sulfopropyl)-5,6,5′,6′-dibenzo-9-ethyloxacarbocyanine and sodium salt of 5,5′-dichloro-3,3′-di(γ-sulfopropyl)-9-ethylthiacarbocyanine form linear rows along the [210] direction on the surface of cubic AgBr microcrystals. These rows of J-aggregates form larger structures, *viz.*, columns with sizes from 20×60 to 30×60 nm,[2] the macrostructures of J-aggregates of oxacarbocyanine being longer than those of J-aggregates of thiacarbocyanine.

The structure of J-aggregates of quino-2,2′-cyanine on the surface of cubic AgBr microcrystals was also studied by this method.[171] The dye molecules in a two-dimensional packing of J-aggregates are inclined at an angle of 10° to the [010] direction. The surpamolecular structure of thiacarbocyanines on AgBr was studied by AFM.[172–174] The differences in the molecular packing of H- and J-aggregates were clearly seen depending on the dye structure. Brickwork- and herringbone-type structures of aggregates were observed for the first time. The brickwork and herringbone structures of H-aggregates are shown in Fig. 19. This figure also shows a model reconstruction of thiacarbocyanine aggregates. Therefore, different aggregate structures, which have been considered earlier in the literature, were confirmed by experimental methods for the first time.

The sizes of columns of J-aggregates determined by AFM agree well with the results of investigation of these aggregates by analytical colour fluorescence electron microscopy (ACFEM).

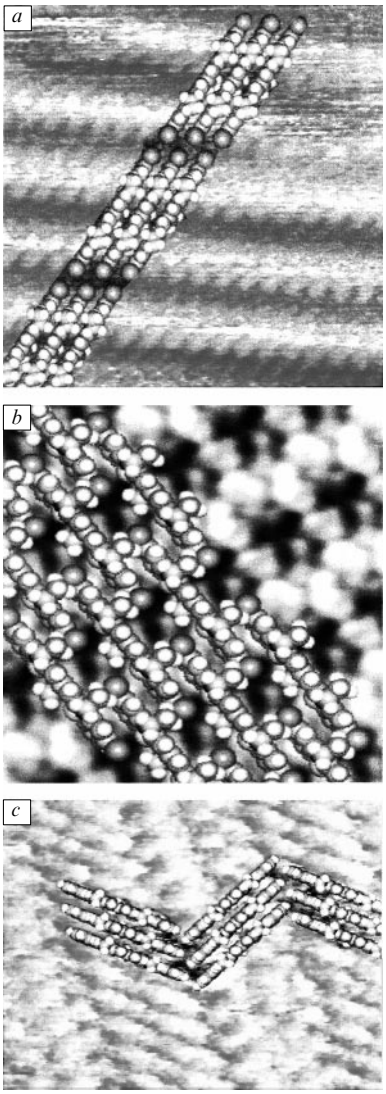


Figure 19. Structures of aggregates of thiacarbocyanine dyes determined by the AFM method;[173]
(*a*) an H-aggregate of 5,5′-dichloro-3,3′-diethyl-9-methylthiacarbocyanine tosylate, an image area is 5.6×5.6 nm^2; (*b*) a brickwork structure of 5,5′-dichloro-3,3′-diethyl-9-ethylthiacarbocyanine tosylate, an image area is 3.6×4.2 nm^2; (*c*) a herringbone structure of 3,3′-dimethyl-4,5,4′,5′-dibenzo-9-methylthiacarbocyanine tosylate, an image area is 4.1×4.5 nm^2.

Studies by ACFEM demonstrated [175] that the dimensions of columns depend on the nature of the dye. The size distribution of J-aggregates of oxa- and thiacarbocyanines depending on the location of J-aggregates on the (100) face of AgBr was also studied by ACFEM.[176] It was found that large J-aggregates are predominantly formed in zones bordering the vertices of microcrystals; large and small J-aggregates, in zones bordering the edges; small J-aggregates, in the middle region of the face. The sizes of aggregates were determined in pixels (1 pixel = 3.3×4.1 nm^2). The sizes of large, medium and small aggregates were 5–6, 3–4 and 1–2 pixels, respectively. J-Aggregates of cyanine dyes on AgBr microcrystals were also studied by ACFEM.[177] The surface area of J-aggregates was $\sim 30 \times 70$ nm^2. The size of J-aggregates increased without change in their number with increasing amount of the adsorbed dye. It was demonstrated that aggregates on the surface of cubic AgBr are extended along the [110] or [210] direction.

The ACFEM method was used to study J-aggregation and the orientation of quino-2,2′-cyanine and oxacarbocyanine on the (100) and (111) surfaces of cuboctahedral AgBr microcrystals.[178] It was found that the luminescence colour of J-aggregates changes under the action of the electron flux during measurements. No differences in luminescence on the (100) and (111) surfaces were revealed. The formation of J-aggregates on different faces of AgHal was revealed from luminscence studies.[178, 179] J-Aggregation of thia- and indocarbocyanine dyes on cubic and planar AgBr microcrystals was investigated by ACFEM.[180] Based on the results of this investigation, it was concluded that the sizes of J-aggregates of 5-substituted of thiacarbocyanines on cubic microcrystals are larger than those of unsubstituted dyes. It was noted that an increase in the sizes of J-aggregates of dyes with time occurs according to the mechanism of Ostwald ripening.

Thus, the structures of J-aggregates in solution and the structures of aggregates adsorbed on the surface of AgHal were studied in depth. The main structures of J-aggregates of cyanine dyes were calculated and determined experimentally. J-Aggregates were demonstrated to be highly organised and their structures are determined by the geometry of the dye molecules, the surface of AgHal microcrystals and the surface concentration of the dye. However, due to a complexity of photographic systems, the aggregate structures formed in a particular photographic emulsion cannot always be determined with high precision. Nowadays, it is impossible to take into account, in full measure, all various interrelating factors in real emulsion systems, the role of the dye structure, the method of the addition of the dye to photographic emulsions, the role of supersensitisers and aggregating additives and the surface state of microcrystals. Nevertheless, the main factors responsible for J-aggregation, which can be used to initiate the formation and control the growth of J-aggregates, were revealed. It is impossible to control these processes without knowledge of the surface state of AgHal emulsion microcrystals.

4. Energy levels of aggregated forms of dyes

The positions of the energy levels of aggregates responsible for their physicochemical properties depend primarily on the electronic structures of individual dye molecules and the mutual geometric arrangement of the molecules in aggregates.

Two π-electrons are located in the highest occupied molecular orbital (HOMO) of a monomeric dye in the ground state. Absorption of a light quantum by a dye without a change in the spin leads to excitation of one π-electron from HOMO to the lowest unoccupied molecular orbital (LUMO) and the molecule is converted into the first excited singlet state (Dy*). The energy of transition from the ground state to the first excited singlet state is equal to the energy difference between LUMO and HOMO. The positions of the energy levels of LUMO (ε_{LUMO}) and HOMO (ε_{HOMO}) relative to the electron bands of AgHal determine the efficiency of spectral sensitisation by a dye.[2, 3]

The positions of the energy levels of organic dyes can be found experimentally and calculated by quantum chemical methods. Since it is difficult to determine the energy levels of dyes adsorbed on AgHal by experimental methods,[3] quantum chemical methods have gained wide acceptance.

First attempts to relate the energy levels (calculated by the Hückel method) of the simplest cyanines to their photographic efficiency were made in the studies.[181, 182] More recently, systematic studies by Tani and Kikuchi [183, 184] and Sturmer and Gaugh [185, 186] were published. The charge distributions in molecules were calculated by semiempirical all-valence-electron methods at the CNDO/2 level and by the Pariser–Parr–Pople method.[187, 188] These methods give satisfactory estimates for the energies of spectral transitions, charge distributions, dipole moments, redox potentials and pK_a of dyes. When studying the excited state, Forster [189] provided a qualitative verification of the spectra of cyanine dyes based on the selection rules for electron transitions. The calculated data were summarised by Kachkovskii.[14, 190]

According to experimental data, the ionisation energies are 4.4–5.9 eV,[191, 192] and the electron affinities are 3.0–3.3 eV.[193]

Experimental methods for the determination of ionisation potentials and electron affinities, which characterise the ground and excited states of adsorbed dyes, are very complicated and give ambiguous results. Electrochemical methods for the determination of reduction and oxidation potentials have gained wide acceptance. These potentials correlate with ε_{LUMO} and ε_{HOMO}, respectively.[3,6,20] The polarographic half-wave reduction ($E^{red}_{1/2}$) and oxidation ($E^{ox}_{1/2}$) potentials of dyes in solution are generally measured. These potentials correlate with ε_{LUMO} and ε_{HOMO}, respectively. The polarographic potentials for different types of dyes vary in the following ranges: $E^{red}_{1/2}$ from -0.6 to -2.2 V and $E^{ox}_{1/2}$ from 0.2 to 1.3 V (relative to a saturated silver chloride electrode).[186,192]

Adsorption of individual dye molecules on AgHal leads to changes in the positions of ε_{LUMO} and ε_{HOMO} because the energy levels of dyes are subjected to the perturbing action of surface defects of the substrate and impurity centres. Sets of values rather than one value are typical of ε_{LUMO} and ε_{HOMO} of adsorbed dyes.[194,195] Consequently, the mean potentials are dealt with. Therefore, the use of polarographic potentials, which are thermodynamic (*i.e.*, mean) values, is quite justified.

Taking into account aggregation, which also leads to changes in the positions of the energy levels, the situation is complicated. Evidently, the positions of the levels ε_{LUMO} and ε_{HOMO} of an aggregated dye relative to the conduction and valence bands of AgHal are of most importance for spectral sensitisation. Calculations of ε_{LUMO} and ε_{HOMO} of aggregates present considerable difficulties because it is necessary to take into account a combination of molecules characterised by a particular electron density distribution, the mutual orientation of the molecules and the influence of the substrate. Hence, the results of all calculations are approximate.

The molecular-exciton theory in the point-dipole approximation gives qualitative estimates of the shifts of the maxima in absorption spectra of J-aggregates with respect to the position of the maximum in the spectrum of the monomer depending on the intermolecular distance in the aggregate, the number of monomers in the aggregate and the packing angle.[33,93] When studying the spectroscopic characteristics of J-aggregates, Kuhn and coworkers[22,162,163] developed a perturbation method based on the Schrödinger equation in the π-electron approximation. The calculations adequately reproduce the bathochromic shifts of absorption bands for one- and two-dimensional brickwork arrangements of molecules.

The energy change in an aggregate depending on the angle α was estimated by the Pariser–Parr–Pople method.[196–198] It was demonstrated that there is a complex correlation between the energy change and the spectral shift. The plot of the energy of the spectral transition has a pronounced minimum at acute angles α for all dyes (Fig. 20). The angle α at the minimum energy of the spectral transition is ~29°, ~24° and ~21° for tri-, penta- and heptamethinecyanines, respectively. For thia-, oxa- and imidacarbocyanines and pinacyanol, the angle α is 19±2°; for pyridocarbocyanine, 22 ± 2°.[198]

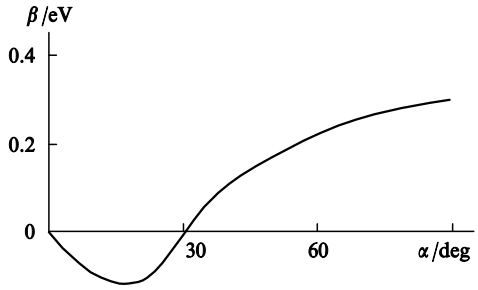


Figure 20. Plot of the energy of the spectral transition *vs.* the packing angle of molecules in J-aggregates for thia-, oxa- and imidacarbocyanines and quino-2,2′-carbocyanine.[198]
The angle α at the minimum energy is 19 ± 2°.

Calculations for narrow J-bands are generally performed with the use of a statistical exciton model,[199–208] according to which the random disorder in the environment is averaged by a moving Frenkel exciton in a J-aggregate. In terms of this model, the electronic structure of isolated polymethine dye molecules involved in J-aggregates is ignored. Egorov[209–212] reduced the problem of electronic excitation of an aggregate to the problem of an elementary electron transfer, which provided an insight into the nature of the J-band.

The determination of the energy levels of J-aggregates by experimental methods presents considerable difficulties. In the review by Dietz,[213] the results of investigations of the energy levels in dye aggregates and the methods for their determination were generalised and analysed. The ionisation potentials, electron affinities and basicities were considered. The difficulties in measuring the redox potentials of dyes adsorbed on silver halide microcrystals were mentioned. It was concluded that the validity of the extrapolation of the polarographic half-wave potentials, which were measured in solution, to adsorbed dyes is not evident.

Nelson[214–216] determined the ionisation energy of pinacyanol adsorbed on CdS as an aggregate. This energy is ~4.5 eV, which is comparable with the ionisation potential of the monomeric form. For some cyanine dyes, the ionisation potentials remain virtually constant (5 eV ± 4%). Dyes differ in the length of the polymethine chain and the nature of heterocyclic groups. Taking into account a small difference in the experimental values, it was concluded that the level ε_{HOMO} changes only slightly upon J-aggregation.

In the review by Dietz,[213] considerable attention was given to investigations of the luminescent properties of adsorbed polymethine dye J-aggregates, which are important for the determination of the energy levels of aggregated dyes. It is commonly accepted that luminescence of aggregates on a substrate is due to bimolecular electron–hole recombination. Usual resonance fluorescence excited in the J-band is observed for adsorbed J-aggregates. Luminescence of J-aggregates and dimers can be explained in terms of the exciton theory of splitting of the excited states due to aggregation.[20] Fluorescence quenching is caused by poly- and monophenols and OH^- ions. The degree of polymerisation of dyes in J-aggregates can be estimated by mathematical processing of fluorescence data.

Cooper demonstrated[217,218] that two bands appear in low-temperature fluorescence spectra of quino-2,2′-cyanines in solution and emulsions. These bands correspond to allowed bands of J-aggregates in the absorption spectrum with maxima at $\lambda_{max_{J_1}}$ = 570.5 nm and $\lambda_{max_{J_2}}$ = 575 nm. Based on a comparison of the intensities of resonance fluorescence of two aggregates adsorbed on a chemically sensitised AgBr emulsion, Cooper concluded that the electron transition to the conduction band of AgBr from photoexcited J_2-aggregates is more efficient than from J_1-aggregates because the latter have a more intense fluorescence band, while the intensity of the adsorption band is lower. Measurements of the microwave photoconductivity of photographic layers performed by Kellog *et al.*[219] confirmed this fact. It was demonstrated that the low efficiency of fluorescence of J_2-aggregates corresponds to the higher efficiency of the formation of electrons in the conduction band in an AgBr emulsion. Due to the presence of impurities, the intensities of two bands change in a different way. The intensity at shorter wavelengths decreases more substantially than that at longer wavelengths. It is assumed that the difference in the photographic activity of these aggregates is associated primarily with the difference in the arrangement of molecules in J-aggregates rather than with the change in the number of molecules in the aggregates.

Based on a comparison of the results obtained in photographic studies of supersensitisation of quino-2,2′-cyanine J_1- and J_2-aggregates upon the addition of oxathiacarbocyanines with different $E^{ox}_{1/2}$ (from 0.54 to 0.98 V *vs.* SCE) and upon fluorescence

quenching in supersensitised aggregates, it was concluded [115–118, 220] that the difference in ε_{HOMO} for J_1- and J_2-aggregates and the positions of ε_{LUMO} in these aggregates relative to each other and relative to the conduction band of AgBr can be rather precisely estimated by combining these methods. An analysis of the dependence of the supersensitisation coefficient on $E^{ox}_{1/2}$ of the supersensitiser demonstrated that the position of ε_{HOMO} for J_2-aggregates can be estimated on the electrochemical potential scale at 0.8 V (*vs.* SCE), whereas the level of ε_{HOMO} of J_1-aggregates is lower. Fluorescence of J_1- and J_2-aggregates at 77 K is excited both in the absorption region of the dye (500 – 530 nm) and in the main absorption region of AgBr (337 nm). This implies that the levels of S_1 (ε_{LUMO}) of aggregates are lower than the conduction band bottom of AgBr. The triplet states of dyes change only slightly upon aggregation,[213] and the splitting of the triplet levels upon dimerisation and polymerisation is small.[34]

In studies by Sviridov and co-workers,[221–223] the changes in the positions of the energy levels of dyes upon J-aggregation were estimated by photochemical oxidation of poly- and monomolecular forms of carbocyanine dyes on the surface of WO_3 films. It was demonstrated that aggregates act as reducing agents for the monomeric form in oxidation of thiacarbocyanine dyes, whereas nonaggregared dyes serve as a reducing agent in the case of imidacarbocyanines. Therefore, the level ε_{HOMO} of thiacarbocyanines increases upon aggregation, whereas the level ε_{HOMO} of imidacarbocyanines decreases. For oxacarbocyanines, the levels ε_{HOMO} of J-aggregates also increase. An increase in the energy levels ε_{HOMO} of thiacarbocyanine J-aggregates compared to the energies of the occupied electronic levels of monomers was observed by Kawasaki *et al.*,[224–226] who used electrochemical oxidation. In the case of J-aggregation, the oxidation potential becomes more negative (by $\sim$0.2 V).

Cramp *et al.*[227, 228] and Ehrlich [229] were the first to study cyanine dye aggregates by flash photolysis. Chibisov *et al.*[230, 231] employed flash photolysis to study the positions of the energy levels of dyes in J-aggregates. It was demonstrated that excitation of dyes to the J-band is accompanied by 'whitening' of this band and the formation of induced short-wavelengths absorption bands belonging to radical dications of dyes followed by band relaxation of J-aggregates. The relaxation rate correlates with $E^{ox}_{1/2}$ of dyes. Therefore, ε_{HOMO} for J-aggregates of different dyes can be related to $E^{ox}_{1/2}$.

Lenhard and Hein [232, 233] performed experimental studies on the changes in the positions of the energy levels (the redox potentials) for J-aggregation of thiadicarbocyanine containing a bridging substituent in the chain. The aggregation state of the dye was varied by introducing a deaggregating agent. An energy level diagram was constructed. According to this diagram, aggregation of thiadicarbocyanine leads to only a weak change in ε_{HOMO}, and the level ε_{LUMO} decreases by 0.32 eV.

In conclusion, let us note that substantial changes in the positions of the levels ε_{HOMO} and ε_{LUMO} upon aggregated adsorption (by about 0.2 – 0.3 eV) explain to a large extent the behaviour of cyanine dye J-aggregates as either sensitisers or desensitisers of silver halides. Hence, to predict and verify the methods for intensification of spectral sensitisation, it is important to know the positions of the energy levels of J-aggregates.

5. Mechanism of the photographic action of dye aggregates

In the pioneering studies performed by Spence and Carroll [234] as well as by West and Carroll,[235] the photochemical activity of dyes was quantiataively estimated and the molecular state was demonstrated to be photochemically active. More recently, Natanson and Klimzo [4, 5] found that the photochemical activity of J-aggregates generally increases as the corresponding band is shifted to longer wavelengths, and the activity of H-bands decreases as the band is shifted to shorter wavelengths. It should be noted that the photochemical activity of J-aggregates of well-aggregating dyes is higher than the activity of the molecular state. As a rule, the sensitising ability of J-aggregates characterised by a narrow band is higher than that of J-aggregates with a broad band.[4]

If J-aggregates are formed on the surface of AgHal microcrystals only at rather high dye concentrations, these aggregates were demonstrated [4, 5] to be photographically less active than monomers. The lower photochemical activity of J-aggregates of some sensitising dyes compared to that of dyes in the M-state is attributed to a higher probability of secondary dye desensitisation and self-desensitisation competing with the formation of a latent photographic image.[6, 80]

Processes responsible for desensitisation lead to a decrease in the intrinsic light sensitivity of photographic emulsion layers. Photoexcitation of dyes also causes desensitisation. This process is referred to as dye self-desensitisation.[3, 6] The difference between dye desensitisation and self-desensitisation is related to the differences in the photoprocesses upon photoexcitation of AgHal and dyes.[6, 236] As a rule, a decrease in the light sensitivity due to self-desensitisation is more pronounced in the region of additional light sensitivity compared to the intrinsic light sensitivity.[6, 236]

Aggregated forms of dyes are characterised by self-desensitisation according to the hole mechanism (type II dye self-desensitisation):[6] recombination of dye holes and photoelectrons trapped on the surface of AgHal microcrystals. These processes are most typical of dye J-aggregates, in which holes are translated to considerable distances. The type II desensitisation process, unlike type II self-desensitisation, involves a larger number of steps (Fig. 21).[6] Photoexcitation of AgHal can result in that some holes are trapped on the surface of AgHal microcrystals by the dye to form dye holes and some holes can be trapped by hole-acceptor impurity centres (see Fig. 21 *a*). The type II self-desensitisation process is, apparently, simpler because dye holes inevitably appear upon spectral sensitisation, *i.e.*, in the case of electron transfer from Dy* to AgHal (see Fig. 21 *b*). Therefore, the number of dye holes can be larger. Hence, the probability of self-desensitisation can be higher than the probability of desensitisation and, as a consequence, its influence on spectral sensitivity can be larger than the influence of desensitisation on intrinsic light sensitivity. Its should be noted that if the level ε_{HOMO} of a dye is lower than or

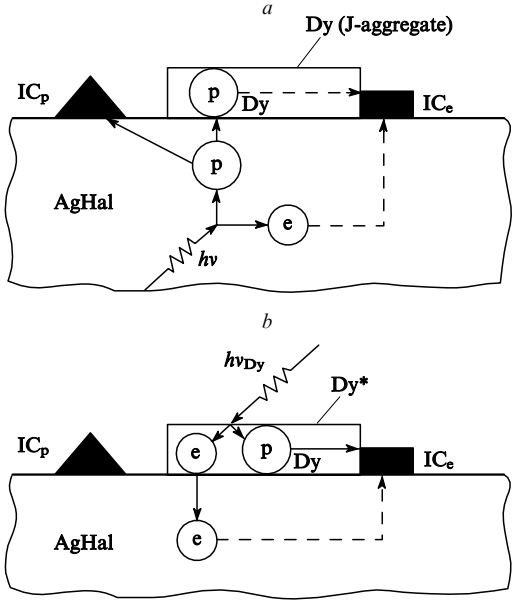


Figure 21. Schemes of desensitisation (*a*) and type II self-desensitisation (*b*).[118]
IC_e is an impurity site as an electron acceptor; IC_p is an impurity site as a hole acceptor; e is a photoelectron; p is a photohole; *hν* is a light quantum absorbed by AgHal; $h\nu_{Dy}$ is a light quantum absorbed by a dye.

close to the valence band top of AgHal, the dye holes can be injected directly to the valence band.

As opposed to type I desensitisation and self-desensitisation according to the electron-acceptor mechanism, no clear dependence for type II desensitisation and self-desensitisation on the polarographic half-wave oxidation potential $E^{ox}_{1/2}$, *i.e.*, the potential of a dye hole, was found.[79, 80, 237] Moreover, structurally similar dyes, which form J-aggregates showing similar absorption maxima and having virtually equal $E^{ox}_{1/2}$, can differ substantially in the desensitising ability and efficiency of spectral sensitisation.[6, 80]

In the studies,[6, 79, 80] the efficiency of type II self-desensitisation was related not only to the energy factor but primarily to the kinetic factor. According to the modern views, sulfite sensitisation affords the $(Ag_2S)_n$ clusters formed at surface defects of AgHal. Silver sulfide clusters form impurity centres, which exhibit properties of either electron acceptors (IC_e) or hole acceptors (IC_p) depending on n, the charge and the location site. Spectral sensitiser molecules are also adsorbed on the surface of AgHal, the molecules being partially self-organised to form rather elongated J-aggregates. According to the kinetic model of densensitisation,[6, 79, 80] type II densensitisation and, particularly, self-densensitisation, should substantially depend on the spatial arrangement of the dye aggregates and the recombination centres at which photoelectrons are located. The rate constant of desensitisation (recombination) according to the hole mechanism (k_d) can be described by the equation

$$k_d = A_d \exp\left(-\frac{\alpha \Delta E^\circ}{RT}\right), \quad (3)$$

where A_d is the frequency factor, α is the coefficient and ΔE° is the electrochemical potential difference between the dye hole and the electron trapped by an impurity centre on the surface of AgHal

$$\Delta E^\circ = E^{ox}_{1/2} - E^\circ_{IC_e}.$$

It should be noted that the rate constant of recombination for organised systems of J-aggregates, unlike stochastic systems in which a dye exists in the molecular state, is more dependent on the frequency factor A_d than on the energy factor (ΔE°). The frequency factor is a function of the distance r between the J-aggregate and the electron-acceptor impurity centre.

If the transfer of a dye hole to IC_e occurs without the involvement of the valence band of AgHal on the surface across the tunnel junctions under a barrier with a width r, then

$$A_d \approx \exp(-r),$$

i.e., the frequency factor strongly depends on r. In addition, this factor is related to the mobility (μ) of dye holes within the aggregate. The latter is determined by the structure of the J-aggregate, primarily, by the interplanar distance between the dye molecules in the aggregate and the packing angle. Consequently,[6]

$$A_d = f(\mu, r).$$

If self-organisation of dye molecules in J-aggregates is hindered, it starts at surface defects of AgHal, including impurity centres, *viz.*, chemical sensitisation products (Fig. 22 *a*). Due to a contact between J-aggregates and IC_e ($r \to 0$), the frequency factor and the recombination rate increase, which is manifested as a considerable dye self-desensitisation. On the contrary, if J-aggregation readily occurs and aggregates can be formed not only at defects of AgHal but also at other sites, the probability of contacts between the aggregates and IC_e decreases, the distance r increases (Fig. 22 *b*) and, as a consequence, the recombination rate decreases. Apparently, the difference in the photographic properties of dyes similar in the structure and energy levels is associated with the topography of aggregates formed on the surface of AgHal. Let us note once again that the probability of type II self-desensitisation, which depends on the dye structure, the habit of AgHal microcrystals, pAg and other factors, can be

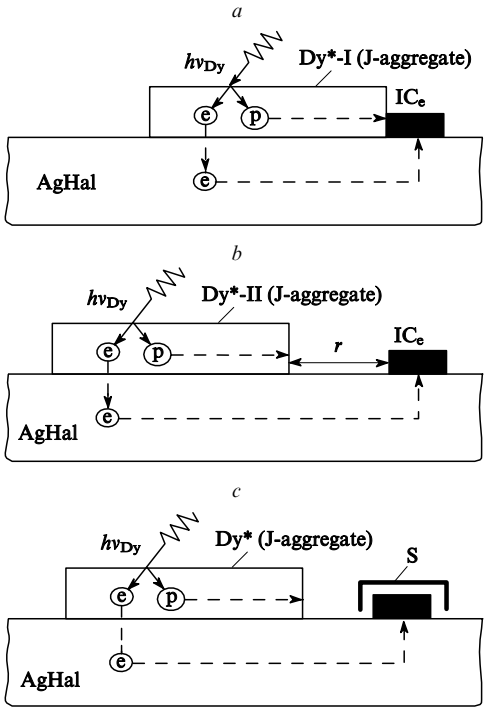


Figure 22. Schemes of self-desensitisation of J-aggregates of dyes (*a*, *b*) and supersensitisation according to the 'isolation' mechanism (*c*).

substantially higher than the probability of desensitisation. Hence, self-desensitisation can to a large degree determine the efficiency of spectral sensitisation of AgHal by aggregating dyes.[6, 80]

The efficiency of spectral sensitisation can be increased with the use of supersensitisers. Over many years, the results of studies on desensitisation and supersensitisation have not been generalised. Shapiro considered [79, 80, 126] a generalised chemical concept of spectral sensitisation, in which particular attention is given to secondary oxidative dye self-desensitisation. According to this concept, supersensitisation is considered as deceleration of secondary dark dye self-desensitisation. There are at least three mechanisms of inhibition of type II hole self-densensitisation: (1) dye hole trapping by a supersensitiser; (2) 'isolation' of a hole from an impurity centre acting as a photoelectron acceptor (IC_e); (3) control over aggregation in such a way as to exclude the possibility of existing contacts between aggregates and IC_e.[126]

The mechanism of dye hole trapping by a supersensitiser (the arbitrary reductive mechanism) was considered in detail by Gilman.[238] This mechanism is most typical of J-aggregating dyes, in which holes can migrate to large distances within the aggregates. A bright example of the supersensitising action of the styryl fragment of 2-(*p*-diethylaminostyryl)benzothiazole on J-aggregates of 1,1′-diethyl-2,2′-cyanine iodide was given in the study.[235] A slight change in the absorption band of J-aggregates in the presence of a supersensitiser led to a sharp increase in the photographic sensitivity (by more than an order of magnitude). Measurements of the photoconductivity of photographic layers also demonstrated a considerable increase in photoconductivity in the case of absorption in the J-band, which is indicative of an increase in the quantum yield of Dy*-derived photoelectrons to the conduction band of AgHal. According to West and Carroll,[235] photoexcitation of J-aggregates gives rise to excitons, whose rate of propagation in the dye layer is so high that the electron transfer to the conduction band of AgHal can be hindered. Hence, excitation is lost due to either thermal energy dissipation or dye fluorescence. The addition of a supersensitiser and inclusion of the latter in J-aggregates hinders exciton motion. Therefore, a super-

sensitiser acts as an exciton trap. Exciton trapping leads to an increase in the probability of electron transfer to AgHal. This phenomenon was considered in more detail by Gilman.[238]

According to Gilman, supersensitisation involves oxidation of a supersensitiser (S) by a photoexcited dye Dy_J^* or a dye hole ($Dy_J^{+\bullet}$)

$$Dy_J^* + S \longrightarrow Dy_J^{-\bullet} + S^{+\bullet}, \quad (4)$$

$$Dy_J^{+\bullet} + S \longrightarrow Dy_J + S^{+\bullet}, \quad (5)$$

resulting in relocation of a hole to the supersensitiser.

Supersensitisation according to reaction (4) gives rise to the radical anion $Dy_J^{-\bullet}$. The level ε_{LUMO} of the electron in $Dy_J^{-\bullet}$ is higher than that in Dy_J^* due to interelectron repulsion of the extra electron. Hence, the probability of electron transfer to the conduction band of AgHal increases and, as a consequence, the efficiency of sensitisation increases. In the case of supersensitisation according to reaction (5), the probability of recombination processes decreases due to removal of a dye hole and, consequently, the spectral sensitivity can increase. For supersensitisation to occur according to the hole-acceptor mechanism, the supersensitiser must be oxidised more readily than the dye. Therefore, the condition for supersensitisation can be written as follows:[238]

$$E^{ox}_{1/2(S)} < E^{ox}_{1/2(Dy)}.$$

The 'isolation' mechanism of supersensitisation [79, 80, 239, 240] involves selective adsorption of organic compounds on IC_e (generally, on Ag_2S centres), isolation of J-aggregates from IC_e and, consequently, a decrease in the probability of recombination processes (see Fig. 22 *c*). Processes according to the 'isolation' mechanism can occur with supersensitisers, which are more difficult to oxidise than dyes,[239] *i.e.*,

$$E^{ox}_{1/2(S)} > E^{ox}_{1/2(Dy)}.$$

Various heterocyclic compounds, which are selectively adsorbed on Ag_2S centres, primarily, the well-known stabiliser 4-hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene, can be used as supersensitisers. Purine bases, for example, guanine and adenine, exert the supersensitising action.[79, 80] Some monomethinecyanines and nullmethinemerocyanines are efficient supersensitisers of the 'isolation' type.

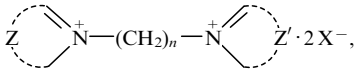
It should be noted that the 'isolation' mechanism substantially differs from the mechanism proposed by Riester.[241] In the supersensitisation model developed by Riester, dye molecules are isolated from the total surface of AgHal, and the 'isolation' mechanism consists in isolating the molecules from the surface impurity centres, which are chemical sensitisation products. This isolation model takes place in core–shell emulsions and Ir^{3+}-doped emulsions. Photoelectron trapping inside AgHal microcrystals hinders electron–hole recombination. Taking into account this fact, desensitisation and self-desensitisation can be substantially decreased.[242–244] The formation of an interlayer formed by a supersensitiser between J-aggregates and impurity centres was observed by luminescence techniques.[245, 246]

Belous and Tolstobrov [246] were the first to find that the intensity of luminescence of the Ag_2S cluster in the IR spectral region decreases in a dye–Ag_2S cluster system upon light absorption by dye J-aggregates adsorbed on Ag_2S. Fano attributed [247] the observed antisensitisation to the antiresonance effect due to interference of the excited states of the dye and Ag_2S in the case of a direct contact between a sensitiser and an impurity centre. Antisensitisation sharply decreases and the intensity of sensitised luminescence of the cluster increases with increasing distance between the Ag_2S cluster and the dye. 4-Hydroxy-6-methyl-1,3,3*a*,7-tetraazaindene [117] and its alkyl analogues, thiamonomethinecyanines, merocyanines, styryl dyes and other compounds showing specific adsorption on Ag_2S centres were used as interlayers between dye aggregates and Ag_2S centres.[248–251]

It was hypothesised [248, 251] that selective adsorption of organic compounds on Ag_2S centres can be due to the presence of 1,3-dipolar structures involving (in the case of thiacyanines) the nitrogen atoms of heterocycles and the carbon atom of the methine group. It should be noted that the distance between the atoms determining the dipole is 2.6 Å, *i.e.*, it is similar to that between the Ag^+ and S^{2-} ions in the Ag_2S clusters.[6, 248–251]

It should be noted that a superadditive increase in the light sensitivity is observed if the two above-mentioned modes of inhibition of type II self-desensitisation occur simultaneously.[79, 80] The superadditive effect of supersensitisation is evidence of the difference between the mechanisms of supersensitisation of photographic layers by two types of compounds in successive steps of dye–hole self-desensitisation. In this case, either dye holes are initially trapped by a readily oxidisable supersensitiser followed by isolation of holes from the photographically active centres with compounds, which are difficult to oxidise and which are adsorbed on these centres, or, alternatively, supersensitisers act in the reverse order.

The third mode of supersensitisation by J-aggregating dyes consists in controlling J-aggregation [126] by adding such organic compounds to a photographic emulsion that either facilitate aggregation or are involved in 'recrystallisation' of aggregates thus facilitating the growth of more ordered structures of J-polymers. As a result, the distance r (see Fig. 22 *b*) can increase (contacts between J-aggregates and IC_e are absent) or more ordered J-aggregates are formed. In the latter, the probability of energy dissipation of photoexcitation of J-aggregates between structurally different aggregates decreases. For example, bis-quaternary salts of heterocyclic bases of the following general formula can act as regulators of J-aggregation:



where Z and Z′ are the groups of atoms, that form the pyridine, quinoline or benzimidazole rings, $n \geqslant 2$ and X^- is the anion.

It was demonstrated [122, 123, 125, 126] that the addition of bis-quaternary salts to a photographic emulsion at concentrations comparable with that of the J-aggregating dye enhances the ability of the latter to form J-aggregates, causes a bathochromic shift of the absorption maximum and leads to an increase in the efficiency of spectral sensitisation. In the studies,[125, 126] the influence of bis-quaternary salts was interpreted as facilitating J-aggregation. Apparently, the fact that the pair positive charges on the nitrogen atoms are not equal to the pair negative charges on the halide ions in the case of adsorption of bis-salts on AgHal microcrystals results in such a relief of the surface potential on the surface of AgHal at which J-aggregation is facilitated not only on defect sites but also on other regions of the surface and which is favourable for ordering of the aggregate structures.

The replacement of the alkyl groups at the nitrogen atoms of cyanine dyes by sulfoalkyl groups [78] (*i.e.*, the transformation into dyes having a betaine structure) facilitates J-aggregation. Apparently, the presence of dipolar betaine structures in anionic dyes can promote both nucleation of J-aggregates on the dipolar surface of AgHal microcrystals (Ag^+ and Hal^- ions) and subsequent aggregate growth.

It is known that J-aggregation is affected by various photographically inactive compounds, for example, ketones, nitriles, aromatic alcohols (phenols), *etc.*, which also cause a bathochromic shift of J-bands and an increase in the efficiency of spectral sensitisation.[126] Generally, the bathochromic shifts of J-bands are related to either a decrease in the packing angle of dye molecules or to an increase in the number of sensitiser molecules involved in aggregates. Both parameters should depend on the aggregation rate. Rapid aggregation should lead to the random formation of particles of different sizes on surface defects of AgHal. Organic compounds cause 'recrystallisation' of J-aggregates. In this case, organic compounds introduced into an emulsion in large amounts

(0.1 – 1.0 mol per mole of AgHal) serve as a medium (a solvent) facilitating 'recrystallisation'. The latter can give rise to more ordered J-aggregates with bathochromically shifted absorption bands and far removed from IC_e ($r > 0$, see Fig. 22 *b*), and lead to an increase in the photographic activity of aggregates. J-Aggregation is often facilitated by an increase in the temperature of a molten emulsion and its storage at high temperature before coating.

The formation of numerous new defects, which stimulate J-aggregate growth at sites that are not bound to impurity centres, on the surface of AgHal microcrystals before the introduction of a spectral sensitiser should facilitate J-aggregation. These numerous defects occur, for example, in the synthesis of AgHal microcrystals with a variable halide composition, particularly, of AgBr(I). Hence, an increase in the concentration of iodide ions in AgBr(I) emulsions to a particular limit generally promotes J-aggregation.[2] This can also account for the influence of the thiocyanate and cyanide ions on J-aggregation. It was demonstrated [252] that the addition of iodide ions to an AgBr emulsion leads to the formation of silver iodide at the vertices and edges of microcrystals, thus promoting J-aggregation. According to the results of the studies,[78, 253] SCN^- and CN^- ions have the same effect. In the studies,[128 – 131] it was also demonstrated that J-aggregation of dyes on AgHal increases in the presence of SCN^-. There are also other procedures for controlling the surface imperfection of AgHal.[125] In addition, J-aggregation can be controlled by decreasing the rate of release of dyes into solution. This can be achieved by adding poorly water-soluble dyes as aqueous sols or by readsorbing dyes from the substrate (SiO_2, *etc.*) on AgHal.[3, 254, 255]

Type I self-desensitisation according to the electron-acceptor mechanism is possible for IR dyes, which form J-aggregates.[6] It is known that the electron affinity of a dye increases with increasing length of the polymethine chain resulting in a considerable decrease in the efficiency of spectral sensitisation.[83, 133] According to the modern views,[6] dyes in the ground state serve as intermediate carriers of electrons to oxygen atoms and protons, *i.e.*, dyes catalyse oxidation by oxygen involving protons of water molecules. The intermediate involvement of dyes in type I self-desensitisation can be determined by such factors as the electron affinity of the molecule and the positive charge of the chromophoric moiety of the dye. In this case, the probability of secondary oxidation processes should increase with increasing electron affinity of dye molecules (which is characterised by the polarographic half-wave reduction potential) and particularly with increasing length of an electron acceptor in aggregates.

The following suggestion was made:[134, 256] if an efficient procedure were available for assembling unstable silver atoms (or subcentres of a latent image) to form stable particles of a latent image during exposure, the spectral sensitivity of a photomaterial would be substantially increased due to a decrease in the contribution of dye self-desensitisation to spectral sensitisation. The main idea of this method is that the chemical enhancement, *i.e.*, the development of a photomaterial already in the step of exposure, is employed. In this case, latensification of a latent image occurs during exposure. For this purpose, it is necessary to provide a reducing medium in the photographic layer by adding a reductone. The algorithm of this process can be as follows: before exposure, *i.e.*, before the formation of catalytic silver particles, a reductone does not reduce AgHal, apparently, due to kinetic factors. However, after blanket exposure and the formation of silver particles, a reductone reduces pre- and subcentres of a latent image to form stable developed centres of a latent image. This can be described by the following processes:

$$Dy^* + AgHal \longrightarrow Dy^{+\cdot} + [AgHal]^-,$$

$$[AgHal]^- + Ag_i^+ \longrightarrow [AgHal/Ag^0],$$

$$[AgHal/Ag^0] + Red \longrightarrow [AgHal/Ag_n^0] + Ox.$$

Ascorbic acid is a natural reductone, which has long been used in photographic processes.[3] The action of ascorbic acid on infrared photographic layers is a bright example of the efficiency of reducing supersensitisers.[233, 257 – 260] Several mechanisms of action of ascorbic acid were described in the literature. It was hypothesised [233] that an IR dye is oxidised on the surface of AgHal to form a radical dication thus enhancing desensitisation according to the mechanism of photoelectron trapping. The authors observed the appearance of a new hypsochromically shifted absorption band of the radical dication of an IR dye, whose intensity decreased in the presence of ascorbic acid. Consequently, ascorbic acid (in the authors' opinion) reduces the radical dications of the dye to the dye in the ground state, which leads to a decrease in desensitisation. According to the above-considered mechanism, the influence of ascorbic acid occurs before the light action.

The influence of ascorbic acid on numerous IR dyes containing polymethine chains of different lengths in an AgBr(I) emulsion was studied in detail.[261] Short-wavelength bands of radical dications were found in none of reflection spectra of the dyes, for which a supersensitising effect of ascorbic acid was observed. Hence, it was concluded that the action of ascorbic acid is not associated with reduction of the desensitising radical dication of the dye. It was suggested [26] that ascorbic acid acts as an inhibitor of dye self-desensitisation immediately after the light step.[261]

Ascorbic acid was demonstrated [134] to be adsorbed on silver sulfide sensitivity centres. Latensification of a latent photographic image under the action of ascorbic acid is efficient because silver particles formed on Ag_2S centres are subjected to the primary enhancement by ascorbic acid. Other reductones responsible for the superadditive effect in the photographic development, such as metol, phenidone, dodecyl gallate, *etc.*, behave analogously. Apparently, their action is also associated with specific adsorption on Ag_2S centres and latensification of a latent photographic image.

A new method of inhibition of type II self-desensitisation according to the hole mechanism was considered.[80, 134, 256] This method is based on the use of a new type of supersensitisers which undergo transformation as a result of oxidation by dye holes accompanied by decomposition of the initial core. This gives rise to a molecule containing a new core, which acts as a reducing agent for AgHal. Chemical transformations of the oxidised form of a supersensitiser lead to the injection of one electron (or several electrons) into AgHal microcrystals, resulting in an enhancement of a latent photographic image. The scheme of the process is as follows:[80]

$$Dy + h\nu \longrightarrow Dy^*,$$

$$Dy^* + AgHal \longrightarrow Dy^{+\cdot} + [AgHal]^-,$$

$$[AgHal]^- + Ag^+ \longrightarrow [AgHal/Ag^0],$$

$$Dy^{+\cdot} + BH \longrightarrow Dy + BH^{+\cdot},$$

$$BH^{+\cdot} + R^- \longrightarrow B^\bullet + HR,$$

$$B^\bullet + [AgHal/Ag^0] \longrightarrow B^{+\cdot} + [AgHal/Ag^0]^-,$$

$$[AgHal/Ag^0]^- + Ag^+ \longrightarrow [AgHal/Ag_2^0],$$

$$B^{+\cdot} + \text{medium} \longrightarrow \text{products},$$

where BH is a supersensitiser and R^- is a base. According to this scheme, the supersensitiser BH is oxidised by a dye hole to form the radical cation $BH^{+\bullet}$, which reacts with the base R^- to give the radical $B^\bullet$. The latter can act as a reducing agent for silver halide, *i.e.*, can inject the second electron into AgHal, resulting in the growth of the centre of a latent photographic image.

The above two-electron scheme was used in the studies.[262 – 264] The formate anion (HCO_2^-) served as a hole acceptor. Oxidative decomposition of organic compounds accompanied by electron injection into AgHal was experimentally performed by Muenter and co-workers.[265 – 271] Carboxy-substituted amines were gener-

ally used as hole acceptors. Decomposition of the resulting radical cations can occur in decarboxylation, deprotonation, C–C bond cleavage, *etc*.

In essence, all the above-considered supersensitisation processes under the action of reductones involve reductive latensification of a latent photographic image. This process can be initiated by either a reductone present in a photographic layer (for example, by ascorbic acid) or a reductone formed upon oxidative decomposition of a supersensitiser.

Nowadays, the unique properties of silver halide as a catalytic light-sensitive system are used in full measure only in the dark step of the photographic process (in the step of development). Nevertheless, the use of the unique catalytic properties of AgHal in the light step of the photographic process (as the 'primary development') holds promise. This strategy of spectral sensitisation would be expected to lead to a considerable increase in the light sensitivity of photomaterials.

Various approaches to the explanation of the photographic action and supersensitisation of polymethine dye aggregates were considered in the literature in sufficient detail. A unified theory of spectral sensitisation was developed. This theory is based on redox reactions in a photographic layer, which occur after dye photoexcitation in the secondary dark steps. Of all aggregated forms, the J-aggregated state of cyanine dyes is the most photographically efficient form.

V. Conclusion

Dye aggregates and, primarily, J-aggregates are nanosize molecular ensembles. Aggregates possess collective properties due to formation of a common π-conjugated system, which is reflected in changes in the electronic levels of dyes involved in aggregates, optical absorption bands and the chemical and photochemical activity. Evidently, all these properties depend on the aggregate structure, which is, in turn, determined by the mode of their formation. Nowadays, the architecture, more precisely, the nanoarchitecture of molecular ensembles of dyes can be considered. As in the traditional architecture, the appearance and functional possibilities of nanoarchitectural ensembles are determined by elements of the nanoarchitecture and their combination. In the nanoarchitecture of molecular ensembles of polymethine dyes, molecules, dimers and larger species serve as such elements. It should be noted that numerous elements are available because the class of polymethine dyes is characterised by a great variety of molecular structures and the diversified optical and electronic properties.[2,3]

The nanoarchitecture of molecular ensembles of polymethine dyes is based on their specific structural features, which determine the tendency of dyes to undergo self-association. A new principle of the construction of complex organised systems from blocks (dimers, which are the simplest organised elements) rather than from individual 'bricks' (molecules) is of particular interest. Presumably, the block principle of construction is widespread in the Nanoworld and occurs in more complicated biological structures

Investigations of molecular ensembles of polymethine dyes belong to the field of nanochemistry and nanotechnology.[272] It should be noted that the notions of nanoscience and nanotechnology are frequently mixed in the literature, although they are obviously different. Molecular ensembles of polymethine dyes are successfully used in nanotechnology for the preparation of photographic materials. Dye J-aggregates have been efficiently used in photographic processes as optical sensors in the spectral sensitisation for approximately seven decades.

Nowadays, in the framework of nanotechnology, aggregates composed of a small number of coloured organic compounds are of particular importance due to the extensive development of optical methods for data recording, processing and reading. In particular, methods for the controlled formation of molecular ensembles of polymethine dyes having desired structures and required optical and electronic properties are of interest for the use in systems of optical conversion of data, including 'optical' computers.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 04-03-32 009).

References

1. H W Vogel *Berichte* **6** 1302 (1873)
2. C K E Mees, T H James *The Theory of the Photographic Process* (3rd Ed.) (New York: Macmillan, 1966)
3. T H James *The Theory of the Photographic Process* (4th Ed.) (London: Macmillan, 1977)
4. S V Natanson, E F Klimzo *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **5** 452 (1960)
5. S V Natanson *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **8** 362 (1963)
6. B I Shapiro *Teoreticheskie Nachala Fotograficheskogo Protsessa* (Theoretical Principles of Photographic Process) (Moscow: Editorial URSS, 2000)
7. S Daehne *Bunsen-Magazin* **4** 81 (2002)
8. E E Jelly *Nature (London)* **138** 1009 (1936)
9. G Scheibe *Angew. Chem.* **49** 563 (1936)
10. S Sheppard *Photogr. J.* **32** 300 (1908)
11. S Sheppard *Proc. R. Soc. London, Ser. A* **82** 256 (1909)
12. S Daehne *Science* **199** 1163 (1978)
13. S Daehne *Photogr. Sci. Eng.* **23** 219 (1979)
14. A D Kachkovskii *Stroenie i Tsvet Polimetinovykh Krasitelei* (Structure and Colour of Polymethine Dyes) (Kiev: Naukova Dumka, 1988)
15. E Daltrozzo, G Scheibe, K Gschwind, F Haimerl *Photogr. Sci. Eng.* **18** 441 (1974)
16. A H Herz *Adv. Colloid Interface Sci.* **8** 237 (1977)
17. A H Herz *Photogr. Sci. Eng.* **18** 323 (1974)
18. E McRae, M Kasha *J. Chem. Phys.* **28** 721 (1958)
19. M Kasha *Physical Processes in Radiation Biology* Vol. 17 (New York: Academic Press, 1964)
20. F Dietz *J. Signalaufzeichnungsmater.* **1** 157 (1973)
21. T Kobayashi (Ed.) *J-Aggregates* (New Jersey, London, Hong Kong: World Scientific Singapore, 1996)
22. V Czikkely, H Forsterling, H Kuhn *Chem. Phys. Lett.* **6** 11 (1970)
23. H Bucher, H Kuhn *Chem. Phys. Lett.* **6** 183 (1970)
24. T Tani *Photographic Sensitivity. Theory and Mechanisms* (New York, Oxford: Oxford University Press, 1995)
25. R Ballard, B Gardner *J. Chem. Soc., B* 736 (1971)
26. F Dietz *Tetrahedron* **28** 1403 (1972)
27. C Reich *Photogr. Sci. Eng.* **18** 335 (1974)
28. V I Avdeeva, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **42** 27 (1997)
29. Z Zhang, J Hao, B Wu, H Yuan *J. Imaging Sci.* **39** 373 (1995)
30. M Iwasaki, K Higashinaka, T Tanaka *J. Soc. Photogr. Sci. Technol. Jpn.* **58** 361 (1995)
31. W West, S Pears *J. Phys. Chem.* **69** 1884 (1965)
32. M Zwick, Y Kuhn *Z. Naturforsch., Sec. A* **17** 411 (1962)
33. E Emerson, M Conlin, A Rosenoff, K Norland, H Rodriguez, D Chin, G Bird *J. Phys. Chem.* **71** 2396 (1967)
34. W West, S Lovel, W Cooper *Photogr. Sci. Eng.* **14** 52 (1970)
35. E Michelbacher *Z. Naturforsch., Sec. A* **24** 790 (1969)
36. V I Avdeeva, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **44** 20 (1999)
37. V I Avdeeva, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **45** 27 (2000)
38. V I Avdeeva, B I Shapiro *Dokl. Akad. Nauk* **368** 68 (1999) [a]
39. G Scheibe, A Vareis, H Ecker *Naturwissenschaften* **25** 474 (1937)
40. T L Penner, D Mobius *Thin Solid Films* **132** 185 (1985)
41. Y Yonezawa, T Miyama, H Ishizawa *J. Imaging Sci. Technol.* **39** 331 (1995)
42. V I Avdeeva, V G Semenkina, B I Shapiro *Khim. Vys. Energ.* **40** (5) (2006) [b]
43. J-M Lehn *Supramolecular Chemistry: Concepts and Perspectives* (Weinheim: VCH, 1995)
44. A Mishra, R K Behera, P K Behera, B K Mishra, G B Behera *Chem. Rev.* **100** 1973 (2000)

45. A K Chibisov, H Gorner, T D Slavnova *Chem. Phys. Lett.* **390** 240 (2004)
46. S Sheppard, A Geddes *J. Am. Chem. Soc.* **66** 1995 (1944)
47. H von Berlepsch, C Bottcher, A Ouart, C Burger, S Daehne, S Kirstein *J. Phys. Chem. B* **104** 5255 (2000)
48. H von Berlepsch, C Bottcher, A Quart, M Regenbrecht, S Akari, U Keiderling, H Schnablegger, S Daehne, S Kirstein *Langmuir* **16** 5908 (2000)
49. C Spitz, S Daehne, A Ouart, H-W Abraham *J. Phys. Chem. B* **104** 8664 (2000)
50. C Spitz, J Knoester, A Ouart, S Daehne *Chem. Phys.* **275** 271 (2002)
51. S Sheppard *Rev. Mod. Phys.* **14** 303 (1942)
52. S M Solovev *Acta Physikochim. USSR* **19** 592 (1944)
53. H O Dickinson *Sci. Ind. Photogr., A* **23** 103 (1952)
54. A V Borin *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **1** 111 (1956)
55. S Boyer, L Pichon, O Degove *J. Chem. Phys.* **62** 301 (1965)
56. H Hermel, A Seeboth *J. Photogr. Sci.* **38** 70 (1990)
57. A N Krasovskii, A I Andreeva, A B Plodistyi, B N Nikolaev *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **42** 69 (1997)
58. V I Avdeeva, B I Shapiro *Dokl. Akad. Nauk* **389** 62 (2003) [a]
59. V I Avdeeva, B I Shapiro *Khim. Vys. Energ.* **39** 1 (2005) [b]
60. E I Mal'tsev, D A Lypenko, B I Shapiro, G Milburn, D Rait, M A Brusentseva, V I Berendyaev, B V Kotov, A V Vannikov *Vysokomol. Soedin., Ser. A* **42** 299 (2000) [c]
61. E I Mal'tsev, D A Lypenko, B I Shapiro, A V Vannikov *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **46** 13 (2001)
62. E I Mal'tsev, D A Lypenko, V V Bobinkin, A R Tameev, S V Kirilov *Appl. Phys. Lett.* **81** 1 (2002)
63. A V Vannikov, A D Grishina, B I Shapiro, L Y Pereshivko, T V Krivenko, V V Savelyev, V I Berendyaev, R W Rychwalski *Chem. Phys.* **287** 261 (2003)
64. A D Grishina, B I Shapiro, L Ya Pereshivko, T V Krivenko, V V Savelyev, V I Berendyaev, R W Rychwalski, A V Vannikov *Vysokomol. Soedin., Ser. A* **47** 285 (2005) [c]
65. K A Kuznetsov, T V Laptinskaya, Yu B Mamaeva, E A Mamchitts, E E Makhaeva, A R Khokhlov, B I Shapiro *Kvant. Elektron.* **34** 927 (2004) [*Quantum Electron.* **34** 927 (2004)]
66. V I Avdeeva, A S Kuch'yanov, A I Plekhanov, Yu L Slominskii, A I Tolmachev, B I Shapiro *Kvant. Elektron.* **33** 539 (2003) [*Quantum Electron.* **33** 539 (2003)]
67. A S Kuch'yanov, R V Markov, A I Plekhanov, A E Simanchuk, V I Avdeeva, B I Shapiro, Yu L Slominskii, A I Tolmachev *Opt. Commun.* **231** 343 (2004)
68. R V Markov, A I Plekhanov, V V Shelkovnikov, J Knoester *Phys. Status Solidi B* **221** 529 (2000)
69. R V Markov, A I Plekhanov, Z M Ivanova, V V Shelkovnikov, J Knoester *NATO Sci. Ser. II: Math. Phys. Chem.* **100** 279 (2003)
70. F A Zhuravlev, N A Orlova, A I Plekhanov, S G Rautian, V P Safonov, V V Shelkovnikov *Pis'ma Zh. Eksp. Teor. Fiz.* **56** 264 (1992) [d]
71. G V Zakharova, A R Kombaev, A K Chibisov *Khim. Vys. Energ.* **38** 211 (2004) [b]
72. K Misawa, H Ono, K Minoshima, T Kobayashi *Appl. Phys. Lett.* **63** 577 (1993)
73. K Misawa, H Ono, K Minoshima, T Kobayashi *J. Lumin.* **60–61** 812 (1994)
74. E Rousseau, M M Koetse, M Van der Auweraer *Photochem. Photobiol.* 395 (2002)
75. M Liu, A Kira *Thin Solid Films* **359** 104 (2000)
76. M Vacha, K Hashizume, T Tani *J. Lumin.* **87–89** 730 (2000)
77. E B Lifshits, D Ya Shagalova, E F Klimzo *Usp. Nauchn. Fotogr.* **22** 103 (1984)
78. S V Natanson, E B Lifshits *Usp. Nauchn. Fotogr.* **17** 23 (1976)
79. B I Shapiro *Usp. Nauchn. Fotogr.* **24** 69 (1986)
80. B I Shapiro *Usp. Khim.* **63** 243 (1994) [*Russ. Chem. Rev.* **63** 231 (1994)]
81. US P. 5296343 (1994)
82. Y Inagaki, T Hioki, T Katoh *J. Soc. Photogr. Sci. Technol. Jpn.* **59** 260 (1996)
83. B I Shapiro, Yu L Slominskii, A Yu Uspenskaya, L I Mikheeva, A G Vakar *Zh. Nauchn. Prikl. Fotogr.* **42** 3 (1997)
84. G de W Anderson, in *Scientific Photography* (Ed. H Souvenir) (London: Pergamon Press, 1962) p. 487
85. V I Avdeeva, B I Shapiro, in *Doklady Mezhdunarodnoi Konferentsii 'Fiziko-khimicheskie Protsessy v Neorganicheskikh Materialakh (FKhP-9)', Kemerovo, 2004* [Reports of International Conference 'Physicochemical Processes in Inorganic Materials (PCP-9)', Kemerovo, 2004] Vol. 1, p. 108
86. L G S Brooker, F L White, D W Heseltine, G H Keyes, S G Dent, E J van Lare *J. Photogr. Sci.* **1** 173 (1953)
87. V A Tkachev, A V Tolmachev, Yu L Slominskii *Ukr. Khim. Zh.* **60** 187 (1994)
88. S E Sheppard, R Lambert, R Walker *J. Chem. Phys.* **9** 96 (1941)
89. A K Chibisov, G V Zakharova, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **40** 9 (1995)
90. I I Levkoev *Usp. Nauchn. Fotogr.* **17** 5 (1976)
91. D M Sturmer, W S Gaugh *Photogr. Sci. Eng.* **19** 273 (1975)
92. D Fry, in *Dye Sensitization* (London: Bressanone Symp. Focal Press, 1970) p. 44
93. G R Bird, K S Norland, A E Rossenoff, H B Michaud *Photogr. Sci. Eng.* **12** 196 (1968)
94. K Meyer *Z. Wis. Photogr.* **52** 170 (1958)
95. H Borginon, V Danckaert *Photogr. Korresp.* **98** 74 (1962)
96. W Vanassche *Photogr. Sci. Eng.* **18** 288 (1974)
97. H Phillippaerts, W Vanassche, F H Claes, H Borginon *J. Photogr. Sci.* **20** 215 (1972)
98. S L Scrutton *J. Photogr. Sci.* **22** 69 (1974)
99. W Vanassche, F H Claes, H Borginon, J Liber *J. Photogr. Sci.* **21** 85 (1973)
100. M K Grechko, S V Natanson, in *Sbornik Nauchnykh Trudov Gosniikhimfotoproekta* (Proceedings of Gosniikhimfotoproekt) (Moscow, 1972) p. 68
101. L N Grishina, E F Klimzo, S V Natanson, in *Sbornik Nauchnykh Trudov Gosniikhimfotoproekta* (Proceedings of Gosniikhimfotoproekt) (Moscow, 1977) p. 75
102. T Tani *Photogr. Sci. Eng.* **18** 215 (1974)
103. E Gunther, E Moisar *J. Photogr. Sci.* **13** 280 (1965)
104. W Markocki *J. Photogr. Sci.* **13** 85 (1965)
105. J M Simson *Photogr. Sci. Eng.* **18** 302 (1974)
106. M Kazmierczak, W Markocki *J. Signalaufzeichnungsmater.* **6** 259 (1978)
107. M Tamura, H Hada *Photogr. Sci. Eng.* **11** 82 (1967)
108. L N Grishina, Candidate Thesis in Chemical Sciences, Gosniikhimfotoproekt, Moscow, 1985
109. N I Sennikova, Candidate Thesis in Chemical Sciences, Gosniikhimfotoproekt, Moscow, 1978
110. N I Sennikova, L G Kuznetsova, S V Natanson *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **20** 404 (1975)
111. V L Zelikman, S V Natanson, E B Kondrat'eva *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **18** 105 (1973)
112. S S Collier, A Herz *Photogr. Sci. Eng.* **16** 413 (1972)
113. W L Gardner, D P Wrathall, A Herz *Photogr. Sci. Eng.* **21** 325 (1977)
114. S Boyer, L Picon *Photogr. Sci. Eng.* **18** 555 (1974)
115. B I Shapiro, L L Mkrtchyan, I M Ratner *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **29** 31 (1984)
116. B I Shapiro, L L Mkrtchyan, A F Peshkin, L G Kurkina *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **32** 358 (1987)
117. B I Shapiro, L L Mkrtchyan, Z I Moskalenko, G P Shumelyak *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **32** 44 (1987)
118. B I Shapiro, E N Sergeeva, A V Butuzova *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **33** 256 (1988)
119. O Riester *Photogr. Sci. Eng.* **13** 13 (1969)
120. L N Grishina, S V Natanson *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **22** 93 (1977)
121. E B Lifshits, S V Natanson, E F Klimzo, E N Sergeeva, I I Levkoev *Sovremennoe Razvitie Metoda Vydeleniya Tverdoi Fazy Fotograficheskikh Emul'sii* (Modern Development of the Method of Separation of Solid Phase of Photographic Emulsions) (Yaroslavl': Verkhnevolzhskoe Izd., 1974)
122. E B Lifshits, L I Kirenskaya, D Ya Shagalova, in *Sbornik Nauchnykh Trudov Gosniikhimfotoproekta* (Proceedings of Gosniikhimfotoproekt) (Moscow, 1984) p. 166

123. E B Lifshits, D Ya Shagalova, N V Kudryavskaya, G N Pyleva, in *Tezisy Dokladov Vsesoyuznoi Konferentsii po Problemam Sozdaniya Sovremennykh Tsvetnykh Kinofotomaterialov, Chernogolovka, 1987* (Abstracts of Reports of the All-Union Conference on Problems of Creation of Modern Colour Cinephoto Materials, Chernogolovka, 1987) p. 43
124. L N Grishina, Y A Breslav, S V Natanson, in *Papers from the ICPS (Rochester 1978), Rochester, 1978* Vol. IV-16, p. 175
125. B I Shapiro, in *Tezisy Dokladov Vsesoyuznoi Konferentsii po Problemam Sozdaniya Sovremennykh Tsvetnykh Kinofotomaterialov, Chernogolovka, 1987* (Abstracts of Reports of the All-Union Conference on Problems of Creation of Modern Colour Cinephoto Materials, Chernogolovka, 1987) p. 45
126. B I Shapiro *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **37** 139 (1992)
127. A Yu Uspenskaya, in *Sbornik Nauchnykh Trudov Gosniikhimfotoproekta* (Proceedings of Gosniikhimfotoproekt) (Moscow, 1993) p. 118
128. A Yu Uspenskaya, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **41** 12 (1996)
129. A Yu Uspenskaya, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **41** 41 (1996)
130. A Yu Uspenskaya, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **44** 29 (1999)
131. A Yu Uspenskaya, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **44** 40 (1999)
132. B I Shapiro, L V Rozhkova *Zh. Nauchn. Prikl. Fotogr.* **46** 1 (2001)
133. L V Rozhkova, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **48** 58 (2003)
134. B I Shapiro, in *Proceedings of International Congress of Imaging Science, Tokyo, 2002* p. 91
135. B I Shapiro, L V Rozhkova, Yu L Slominskii, A I Tolmachev *Khim. Vys. Energ.* **38** 371 (2004) [b]
136. M Kawasaki, S Aoyama, in *Proceedings of International Symposium on Silver Halide Technology, Ventura, USA 2004* p. 169
137. A Fadeev, B I Shapiro, in *Proceedings of IS&T-2000 SPSTJ's Conference, Quebec, Canada, 2000* p. 132
138. A A Fadeev, A F Mironov, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **46** 11 (2001)
139. M Kawasaki, H Inokuma, in *Proceedings of International Congress of Imaging Science, Antwerpen, 1998* Vol. 1, p. 496
140. N Tyutyulkov, F Dietz *Z. Phys. Chem. (Leipzig)* **258** 380 (1977)
141. F D Saev, G R Olin, S R Turner, J F Yanus, D J Sandman *Photogr. Sci. Eng.* **22** 129 (1978)
142. H Stiel, W Becker, W Freyer, K Teuchner, S Daehne, in *Tezisy Dokladov Mezhdunarodnogo Simpoziuma po Fotograficheskim Protsessam, Tbilisi, 1984* (Abstracts of Reports of International Symposium on Photographic Processes, Tbilisi, 1984) p. 158
143. W Hoppe *Kolloidn. Zh.* **101** 300 (1942)
144. G Scheibe, St Harwig, R Muller *Z. Elektrochem.* **49** 383 (1943)
145. G Scheibe *Z. Elektrochem.* **52** 283 (1948)
146. A E Rosenoff, V K Walworth, G R Bird *Photogr. Sci. Eng.* **14** 328 (1970)
147. W E Gray, W R Brewer, G R Bird *Photogr. Sci. Eng.* **14** 316 (1970)
148. K Vivan, V K Walworth, A E Rosenoff, G R Bird *Photogr. Sci. Eng.* **14** 321 (1970)
149. K S Norland, A Ames, T Taylor *Photogr. Sci. Eng.* **14** 295 (1970)
150. G R Bird *Photogr. Sci. Eng.* **15** 134 (1971)
151. D L Smith *Photogr. Sci. Eng.* **16** 329 (1972)
152. D L Smith *Photogr. Sci. Eng.* **18** 309 (1974)
153. E Ticken *J. Photogr. Sci.* **21** 11 (1973)
154. V J Saunders, S P Lovell *Photogr. Sci. Eng.* **24** 171 (1980)
155. J E Maskasky *J. Imaging Sci. Technol.* **35** 29 (1991)
156. T Tani, S Kikuchi *Bull. Soc. Photogr. Sci. Technol. Jpn.* **17** 1 (1967)
157. T Tani, S Kikuchi *Bull. Soc. Photogr. Sci. Technol. Jpn.* **18** 1 (1968)
158. B Zuckerman *Photogr. Sci. Eng.* **14** 336 (1970)
159. B Levy, N Mattucci *Photogr. Sci. Eng.* **14** 308 (1970)
160. D Mastropaolo, J Potenza, G R Bird *Photogr. Sci. Eng.* **18** 450 (1974)
161. W Pandolfe, G R Bird *Photogr. Sci. Eng.* **18** 340 (1974)
162. H Kuhn *Pure Appl. Chem.* **27** 421 (1971)
163. H Kuhn, D Mobius *Angew. Chem.* **83** 672 (1971)
164. R Steiger, R Kitzing, R Hagen *J. Photogr. Sci.* **22** 151 (1974)
165. T Tani, T Suzumoto, K Kemnitz, K Yoshihare *Fujifilm Research Development* **39** 32 (1994)
166. T Tani, T Matsubara *J. Imaging Sci. Technol.* **37** 585 (1993)
167. T Tani, Y Sanjo *J. Appl. Phys.* **69** 4391 (1991)
168. T Tani, T Matsubara *J. Imaging Sci. Technol.* **38** 495 (1994)
169. H Asanuma, T Tani *J. Phys. Chem. B* **101** 214 (1997)
170. H Saijo, T Isshiku, M Shiojiri, S Watanabe, T Tani, in *Proceedings of International Congress of Imaging Science, Rochester, USA, 1994* Vol. 1, p. 147
171. K Suzyki, H Nozoye *J. Soc. Photogr. Sci. Technol. Jpn.* **59** 321 (1996)
172. G Janssens, J Gerritsen, H van Kempen, P Callant, G Deroover, D Vandenbroucke, in *Proceedings of International Congress of Imaging Science, Antwerpen, 1998* Vol. 1, p. 202
173. G Janssens, F Touhari, J Gerritsen, H van Kempen, P Callant, G Deroover, D Vandenbroucke *Chem. Phys. Lett.* **344** 1 (2001)
174. F Touhari, E Stoffels J Gerritsen *Appl. Phys. Lett.* **79** 527 (2001)
175. H Saijo, M Shiojiri *J. Imaging Sci. Technol.* **41** 266 (1997)
176. H Saijo, T Isshiki, M Shiojiri, S Watanabe, T Tani, in *Proceedings of International Congress of Imaging Science, Rochester, USA, 1994* Vol. 1, p. 142
177. H Saijo, T Isshiki, M Shiojiri, H Ohtani, G Ning, K Ogawa *J. Imaging Sci. Technol.* **37** 34 (1993)
178. H Saijo, T Isshiki, M Shiojiri, G Ning, K Ogawa *J. Imaging Sci. Technol.* **38** 217 (1994)
179. H Saijo, T Isshiki, M Shiojiri, S Watanabe, T Tani, K Ogawa *J. Imaging Sci. Technol.* **39** 539 (1995)
180. W F Zhao, H Saijo, Y Kobayshi, M Shiojiri, W P Yan, B X Peng *J. Imaging Sci. Technol.* **42** 144 (1998)
181. S Daehne, in *Dye Sensitization: Symposium Bressanone* (London: Focal Press, 1970) p. 69
182. S Daehne *Z. Wiss. Photogr. Photophys. Photochem.* **59** 113 (1965)
183. T Tani *J. Photogr. Sci.* **19** 161 (1971)
184. T Tani, S Kikuchi *Photogr. Sci. Eng.* **11** 129 (1967)
185. D M Sturmer, W S Gaugh *Photogr. Sci. Eng.* **17** 146 (1973)
186. D M Sturmer, W S Gaugh *Photogr. Sci. Eng.* **19** 344 (1975)
187. Y Ferre, H Larive, E J Vincent *Photogr. Sci. Eng.* **18** 457 (1974)
188. K-D Nolte, S Daehne *J. Prakt. Chem.* **318** 993 (1976)
189. T Forster *Fluorescence Organischer Verbindungen* (Gottingen: Vandenhoest und Ruprecht, 1951)
190. A D Kachkovskii *Usp. Khim.* **66** 715 (1997) [*Russ. Chem. Rev.* **66** 647 (1997)]
191. R C Nelson *J. Photogr. Sci.* **20** 211 (1972)
192. T H James *Photogr. Sci. Eng.* **16** 120 (1972)
193. J M Trusty, R C Nelson *Photogr. Sci. Eng.* **16** 421 (1972)
194. S Daehne, O Gurtler *J. Prakt. Chem.* **315** 786 (1973)
195. R C Nelson, P A Yianoulis *Photogr. Sci. Eng.* **22** 17 (1974)
196. F Dietz, H Kohler *J. Prakt. Chem.* **313** 1101 (1971)
197. F Dietz, C Glier *Z. Chem.* **12** 229 (1972)
198. F Dietz, K J Passler *J. Signalaufzeichnungsmater.* **1** 57 (1973)
199. E W Knapp *Chem. Phys.* **85** 73 (1984)
200. E W Knapp, P O J Scherer, S F Fischer *Chem. Phys. Lett.* **111** 481 (1984)
201. H Fidder, J Terpstra, D A Wiersma *J. Chem. Phys.* **94** 6895 (1991)
202. H Fidder, J Knoester, D A Wiersma *J. Chem. Phys.* **95** 7880 (1991)
203. A A Bagatur'yants, V V Egorov, D V Makhov, M V Alfimov *Dokl. Akad. Nauk* **337** 615 (1994) [a]
204. D V Makhov, V V Egorov, A A Bagatur'yants, M V Alfimov *Chem. Phys. Lett.* **246** 371 (1995)
205. D V Makhov, V V Egorov, A A Bagatur'yants, M V Alfimov *J. Lumin.* **72–74** 439 (1997)
206. D V Makhov, V V Egorov, A A Bagatur'yants, M V Alfimov *Zh. Fiz. Khim.* **71** 1805 (1997) [e]

207. D V Makhov, V V Egorov, A A Bagatur'yants, M V Alfimov *Mater. Sci. Eng.* **5** 311 (1998)
208. D V Makhov, V V Egorov, A A Bagatur'yants, M V Alfimov *J. Chem. Phys.* **110** 3196 (1999)
209. V V Egorov *Chem. Phys. Lett.* **336** 284 (2001)
210. V V Egorov *Chem. Phys.* **269** 251 (2001)
211. V V Egorov *J. Chem. Phys.* **116** 3090 (2002)
212. V V Egorov, Doctoral Thesis in Physical and Mathematical Sciences, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, 2004
213. F Dietz *J. Signalaufzeichnungsmater.* **6** 245 (1978)
214. R C Nelson *J. Opt. Soc. Am.* **55** 897 (1965)
215. R C Nelson *J. Mol. Spectrosc.* **23** 213 (1967)
216. R S Nelson *J. Opt. Soc. Am.* **51** 1186 (1961)
217. W Cooper *Photogr. Sci. Eng.* **17** 217 (1973)
218. W Cooper *Chem. Phys. Lett.* **7** 73 (1970)
219. L M Kellog, N B Liebert, T H James *Photogr. Sci. Eng.* **16** 110 (1972)
220. V M Belous, V I Tolstobrov, B I Shapiro *Opt. Spektroskop.* **49** 532 (1980) [f]
221. D V Sviridov, A I Kulak *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **32** 45 (1987)
222. D V Sviridov, A I Kulak, B I Shapiro *Khim. Vys. Energ.* **24** 151 (1990) [b]
223. D V Sviridov, B I Shapiro, A I Kulak *J. Photochem. Photobiol. A* **67** 377 (1992)
224. M Kawasaki, T Sato, in *International Symposium on Silver Halide Technology, Quebec, Canada, 2000* p. 95
225. M Kawasaki, T Sato *J. Phys. Chem. B* **105** 796 (2001)
226. M Kawasaki, T Sato, M Iwasaki, in *Proceedings of International Congress of Imaging Science, Tokyo, 2002* p. 89
227. J H W Cramp, G C Terry, F W Willets *J. Photogr. Sci.* **21** 101 (1973)
228. J H W Cramp, G C Terry, F W Willets *Photogr. Sci. Eng.* **18** 90 (1974)
229. S H Ehrlich *Photogr. Sci. Eng.* **18** 179 (1974)
230. A K Chibisov, G V Zakharova, A S Murakhovskaya, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **38** 59 (1993)
231. A K Chibisov, G V Zakharova, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **40** 39 (1995)
232. J R Lenhard, B R Hein *J. Imaging Sci. Technol.* **38** 129 (1994)
233. J R Lenhard, B R Hein *J. Phys. Chem.* **100** 17287 (1996)
234. J Spence, B H Carroll *J. Phys. Colloid Chem.* **52** 1090 (1948)
235. W West, B H Carroll *J. Chem. Phys.* **19** 417 (1951)
236. T H James *Photogr. Sci. Eng.* **18** 100 (1974)
237. B I Shapiro *Usp. Khim.* **66** 278 (1997) [*Russ. Chem. Rev.* **66** 255 (1997)
238. P B Gilman *Photogr. Sci. Eng.* **18** 418 (1974)
239. B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **45** 67 (2000)
240. B I Shapiro *J. Imaging Sci. Technol.* **46** 89 (2002)
241. O Riester *Photogr. Sci. Eng.* **18** 295 (1974)
242. P B Gilman *J. Photogr. Sci.* **31** 185 (1983)
243. F J Evans, P B Gilman *Photogr. Sci. Eng.* **19** 333 (1975)
244. J M Simson, W S Gaugh *Photogr. Sci. Eng.* **19** 339 (1975)
245. V M Belous, V I Tolstobrov, B I Shapiro *Usp. Nauchn. Fotogr.* **22** 125 (1984)
246. V M Belous, V I Tolstobrov *Opt. Spektroskop.* **50** 682 (1981)
247. U Fano *Phys. Rev.* **124** 1866 (1961)
248. B I Shapiro, L V Tolstova, Yu L Slonimskii, A D Kachkovskii *Zh. Nauchn. Prikl. Fotogr.* **40** 52 (1995)
249. L V Tolstova, N N Pomanov, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **40** 68 (1995)
250. L V Tolstova, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **39** 18 (1994)
251. B I Shapiro *J. Imaging Sci. Technol.* **43** 94 (1999)
252. R Steiger, J N Albischer, E Haselbach *J. Imaging Sci.* **35** 1 (1991)
253. J E Maskasky *J. Imaging Sci.* **32** 160 (1988)
254. I M Zul', G D Kovshulya, M N Ushomirskii, in *Tezisy Dokladov V Sympoziuma 'Fizika i Khimiya Polimetinovykh Krasitelei', Chernogolovka, 1989* (Abstracts of Reports of the Vth Symposium 'Physics and Chemistry of Polymethine Dyes', Chernogolovka, 1989) p. 210
255. US P. 5436112 (1995)
256. B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **47** 11 (2002)
257. US P. 3695888 (1972)
258. US P. 3809561 (1974)
259. US P. 4897343 (1990)
260. US P. 5037734 (1991)
261. I M Popov, B I Shapiro *Zh. Nauchn. Prikl. Fotogr.* **46** 20 (2001)
262. M Treguer, R De Keyzer, H Remita, J Belloni, in *Proceedings of International Congress on Imaging Science, ICPS'98, Antwerpen, 1998* Vol. 1, p. 243
263. J Belloni, M Treguer, H Remita, R De Keyzer *Nature (London)* **402** 865 (1999)
264. Eur. P. 972028970 (1997)
265. A A Muenter, J R Lenhard, S Y Farid, S A Godleski, P A Zielinski, I R Gould, in *Proceedings of International Symposium IS&T/SPSTJ's, Quebec, Canada, 2000* p. 209
266. I R Gould, J R Lenhard, A A Muenter, S A Godleski, S Y Farid *J. Am. Chem. Soc.* **122** 11934 (2000)
267. US P. 5747235 (1998)
268. US P. 5747236 (1998)
269. US P. 5994051 (1999)
270. US P. 6010841 (2000)
271. US P. 6054260 (2000)
272. A L Buchachenko *Usp. Khim.* **72** 419 (2003) [*Russ. Chem. Rev.* **72** 375 (2003)]

[a] — *Dokl. Chem. (Engl. Transl.)*
[b] — *Chem. High Energ. (Engl. Transl.)*
[c] — *Polym. Sci. (Engl. Transl.)*
[d] — *J. Exp. Theor. Phys. Lett. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Opt. Spectroscop. (Engl. Transl.)*