

Kinetic Study of the Ultrafast Electron Transfer from Sensitized Dyes to Silver Halide Microcrystals

Shaopeng Yang, Shanshan Fan, Chunlei Li, Xiaowei Li, Guangsheng Fu, College of Physics Science and Technology, Hebei University, Baoding 071002, China

Abstract

Direct measurements of the dynamics of photo-induced electrons in AgBr photographic system sensitized by dye was performed using picosecond time-resolved fluorescence spectroscopy. The dependence of the electron transfer rate on different condition and the microcosmic mechanism of electron transfer were analyzed. The fluorescence decay curves of J-aggregation on both the cubic and tabular AgBr grains (T-grains) were gained with different dye concentration. These curves are fitted well by a sum of double exponential functions, which are consisted of a fast and a slow component.

1 Introduction

It is generally accepted that spectral sensitization is realized by the electron transfer mechanism presented by Gurney and Mott. Namely, photo-induced electron transfers from excited dye to conduction band (CB) of silver halide to combine with interstitial silver ion to form silver spot of latent-image. To explain the essential process of spectral sensitization and enhance sensitization efficiency, the detection of fluorescence decay lifetime is important. Two techniques are usually used, including time-correlation single photo count technique (TCSPC) and high-speed streak photography technique (Streak Camera). T.Tani¹⁻² et al in Japan and Joseph M. Lanzafame³ et al in America investigated sensitization process of silver halide system using TCSPC. With the improvement of laser source and other experiment conditions and equipments, Streak Camera has developed greatly in the last several decades. T.Tani and his co-workers have performed dynamics study of silver halide sensitization with time resolve rate larger more than 20 picosecond⁴⁻⁵. The time resolve rates have both reached to picosecond. TCSPC can be used widely, but its time resolve rate is larger than 20~50 picoseconds. And the full wave at half maximum (FWHM) of instrument response is less than 50 picosecond. In our work, Streak Camera was used to measure time-resolved fluorescence spectrum with the time resolve rate of 5ps.

2 Experiment

2.1 Preparation of Sample

The emulsions were composed of the suspension of AgBr grains in aqueous gelatin solution, and prepared by the controlled double-jet precipitation method. Edge lengths of the AgBr grains were 0.4 μ m for cubic grains and 1.7 μ m for tabular grains. Values of pH and pBr of the above emulsions were 6.4 and pBr 2.8, respectively. The added amounts of dye methanol solution with concentration 2g/L were 2, 3, 4, 5 and 10mL for T-grains and cubic grains gelatin emulsions, both containing 5g AgBr (AgBr is 2.78mmol and gelatin 4.5g). Dye concentration contrasted with

AgBr was 2.26, 3.38, 4.51, 5.64 and 11.28mmol/mol, respectively. The environment temperature was 45°C during the preparation of samples. The above-state emulsions were agitated for 30 minute to make dye form J-aggregate on AgBr grains. Cyanine dye used in our work is entitled dye 55026.

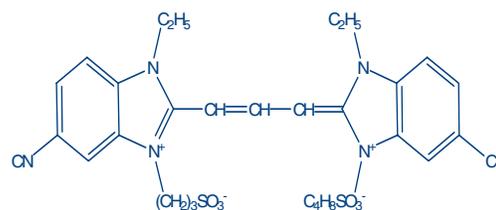


Figure 1. Molecular structure of dye 55026

2.2 Experiment Setup

A Millennia laser was used to pump a mode-locked Ti:sapphire laser Tsunami. Briefly, pulses of 100 fs duration with 8nJ/pulse energy and 800nm wavelength at a repetition rate of 82MHz were generated and amplified in a spitfire regenerative amplifier pumped at 527nm by an Nd: YL laser. The output energy of the spitfire was typically 600 μ J. Then the laser was tuned in optical parameter amplifier (OPA). An electron signal of 1 KHz given by the regenerative amplifier created a gate pulse through a delay Dly1. And the gate pulse chose an electric signal of 82MHz created by a photo-junction diode, which gave a scan signal through another delay Dly2 triggered off a periodicity saw-shaped high voltage putting on the deflexion electric field of Streak Camera. This caused different shifts of photoelectron generated by the excitation of fluorescence.

3 Results

The electron transfer and sensitization efficiency of spectral sensitization can be discussed by the fluorescence emission of dye on silver halide grains. The fluorescence decay of J-aggregate and monomer on AgBr grains surface appears to be very fast and nonexponential. But can be fitted by a double-exponential function.

From Figure2, 3 and Table.1, it is showed clearly that the average fluorescence decay lifetime (τ_{ave}) of J-aggregate on both cubic grains and T-grains is shorter than that of dye monomer. The later is 40.01ps, and the former is less than 10ps for cubic grains and 18ps for T-grains. Especially the faster decay component becomes shorter markedly. This confirms assuredly that electron transfer takes place from excited J-aggregation to conduction band

Table1. Time-resolved fluorescence decay component with double-exponential decay fit (τ_1, τ_2, A_1, A_2) in ps. $\tau_{ave} = (A_1\tau_1 + A_2\tau_2) / (A_1 + A_2)$, $k_{ave} = \tau_{ave}^{-1}$, C stands for cubic grains and T for T-grains. The dye concentration unit is mmol/mol.

Dye	$A_1(\%)$	τ_1	$A_2(\%)$	τ_2	τ_{ave}	k_{ave}
C-2.26	80.4	4.6	19.6	14.1	6.462	0.155
C-3.38	70.1	4.1	29.9	12.9	6.731	0.149
C-4.51	69.2	5.8	30.8	11.9	7.679	0.130
C-5.64	70.4	5.3	29.6	13.9	7.846	0.127
C-11.28	67.5	4.9	32.5	14.8	8.118	0.123
T-2.26	99.4	12.1	0.6	931.6	17.617	0.057
T-3.38	99.0	10.4	1.0	384.3	14.139	0.071
T-4.51	99.6	9.3	0.4	819.7	12.542	0.054
T-5.64	64.8	2.37	35.2	12.6	5.971	0.167
T-11.28	67.9	2.44	32.1	12.1	5.541	0.180

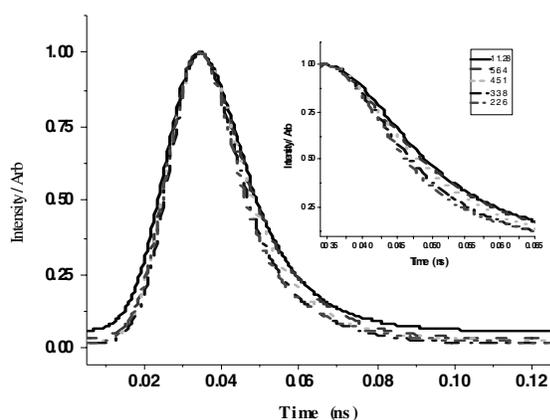


Figure 2. The fluorescence decay dynamics curves of J-aggregate on cubic grains with different concentration

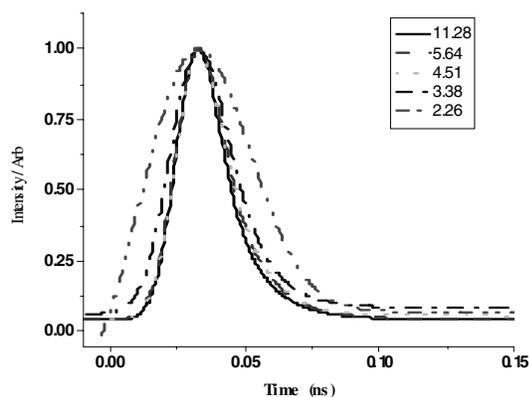


Figure3. The fluorescence decay dynamics curves of J-aggregate on T-grains with different concentration

(CB) of AgBr. The course competes with the fluorescence decay, which makes the fluorescence lifetime shorter and decay faster. Because of larger amplitude (76~89%) and larger quantum yield of electron transfer, the fast decay component should be mainly attributable to the electron transfer from excited J-aggregation to CB of AgBr. At low dye concentration (<4.51mmol/molAg), the electron transfer rate of AgBr T-grains is shorter than that of cubic grains and the sensitization efficiency of dye-55026 for T-grains is lower than that for cubic grains. As the increase of dye concentration, the fluorescence decay for cubic grains has no obviously change. But it is obviously for T-grains. The fluorescence decay lifetime is 12.1ps at 2.26 mmol/molAg and 2.4ps at 11.28mmol/molAg. k_{ave} increases to 0.180ps^{-1} from 0.042ps^{-1} and τ_{ave} reduces to 5.541ps from 23.753ps. The former is 5 times to the later. So the electron transfer rate from excited dye to CB of AgBr competing with the fluorescence emission becomes faster. The sensitization efficiency is higher for T-grains than that for cubic grains.

4 Conclusions

In our work, photo-introduced electron transfer from excited dye-55026 to AgBr cubic grains has been described at different dye concentration. Some information about the dependence of electron transfer and relative quantum efficiency of spectral sensitization was present. The fluorescence decay curves of monomer and J-aggregate of dye are fitted well with a double exponential function. The decay rate of J-aggregate is faster than that of monomer, and the fluorescence lifetime becomes shorter. The fast decay can be mainly attributable to the electron transfer from excited dye J-aggregation to CB of AgBr. As the increase of dye concentration, the sensitization efficiency of Dye-55026 on T-grains is higher than that on cubic grains. It is showed that the spectral sensitization has strong dependence on dye concentration.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 60478033), and the Doctor Foundation of Hebei Province of China (Grant No. B2003119). The authors thank Mr. Yishi Wu, Xiaohui Zhao and Professor Jianping Zhang and Xicheng Ai for their valuable discussion and able technical assistance.

Reference

1. Klaus Kemnitz, Keitaro Yoshihara, Tadaaki Tani. J. Phys. Chem. 94, 3099-3104, 1990.
2. Tadaaki Tani, Takeshi Suzumoto, Klaus Kemnitz, et al. J. Phys. Chem. 96,2778-2783, 1992.
3. Joseph M. Lanzafame, Annabel A. Muentner, Donald V. Brumbaugh. Chem. Phys. 210, 79-89, 1996.
4. Masanao Tanaka, Norihito Nakazawa, Ikuzo Tanaka. Chemical Physics 97,457-463, 1985.
5. Kenji Takahashi, Kinichi Obi, Ikuzo Tanaka, Tadaaki Tani. Chem. Phys. Lett. 154(3), 223-227, 1989.

Molecular Ensembles of Polymethine Dyes

B. I. Shapiro, Scientific Centre of NIIKHFOTOPROEKT, Moscow, Russia

Abstract

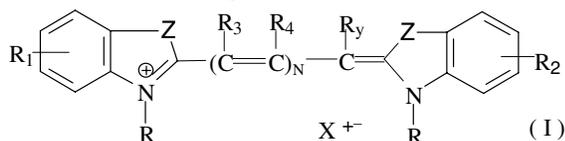
On the basis of studying of a equilibrium between dimers and J-aggregates of cyanine dyes the new mechanism of formation of J-aggregates from dimers is proposed. It was concluded that a method of "block building" of J-aggregates from dimers are the most preferable for construction of "ideal" J-aggregates of the same size (monostructural J-aggregates). Use of the method of the "block building" are obtained the mixed J-aggregates and "heterocontact dimers" from cyanine dyes with a various length of the polymethine chain.

Introduction

The classical photographic process on a basis AgHal is a vivid example of real nanotechnology. To spectral sensitization of AgHal apply nanoparticles of polymethine dyes - J-aggregates. Aggregation of cyanine dyes is a bright example of self-organizing of matter. J-aggregates of dyes represent nanocrystalline structures with a pronounced quantum-size property. Formation of collective π -conjugated system markedly affects the electronic structure, absorption spectra, and photochemical behavior of aggregated dyes [1]. The keen interest to the complex organized structures made from organic molecules, for example, to the J-aggregates of cyanine dyes, is caused, first of all, that use of such structures is perspective for processing and storages of the great mass of information. Just such way is used in the nature. A prominent example is reliable information libraries in the form of DNA used in live organisms. Now J-aggregates are investigated in electroluminescent layers [2] and in systems with nonlinear optical properties [3].

Propensity to J-aggregation of cyanine (or polymethine) dyes depends on a dyes structure: rigid planar structure of chromophore part of molecules and alternation of a π -charge along of a polymethine chain of a dye [4]. Aggregation, as a rule, is facilitated on a surface of a substrate and first of all on AgHal microcrystals [5,6].

It is necessary to note that as a rule J-aggregates of cationic cyanines the structure I (R=Alk) grow in solutions from separate molecules. The chaotic, uncontrolled process resulting in formation of J-aggregates consisting of various number (n) of molecules and then colloid particles [7].



where Z = O, S, NH, -CH=CH-, etc.; R is alkyl, sulfoalkyl; R₁, R₂, R₃, R₄ and R_y are various substitutes; N is 0, 1, 2, 3; X⁺ is counterion.

As have shown, anionic dyes with sulfoalkyl substitutes at heterocycles nitrogen atoms form dimers in water solutions [7]. Apparently, stability of dimers of anionic cyanine dyes is defined by significant intermolecular Coulomb's interaction between a sulfogroup of one molecule and the positive charge located on chromophore of another ones.

Formation of J-aggregates from dimers

In water solutions from dimers thiamono-, tri- penta- and heptamethine cyanines (Z=S, N=0, 1, 2, 3) are obtained J-aggregates of dyes. It is shown [7,8] that at increase of dyes concentration and at lowering of temperature dimers of anionic dyes form J-aggregates. These processes are equilibrium and reversible. On the Fig. 1 an equilibrium between dimers (D) and J-aggregates of triethylammonium salt of 3,3'-di-(γ -sulfo-propyl)-4,5-benzo-5'-Cl-thiamonomethinecyanine (dye-1) is shown. The equilibrium is thermodynamic reversible and spectral curves pass through isobestic point. An equilibrium $mD \leftrightarrow J$ is investigated in the range of the concentrations between 10^{-4} and 10^{-5} Mol/L. At decrease of temperature and increase of concentration the dyes the equilibrium is shifted to J-aggregates.

The size of J-aggregates was determined from the $\log(nC_D) - \log C_D$ plots [8]. The slope of the straight line gives the number of dimers (m) in one J-aggregate. For dye-1 $m=2$, that is, the J-aggregate consists from two dimers or four monomer molecules. Earlier, formation of J-aggregates by four molecules was reported for imidacarbocyanine (from monomers) [5].

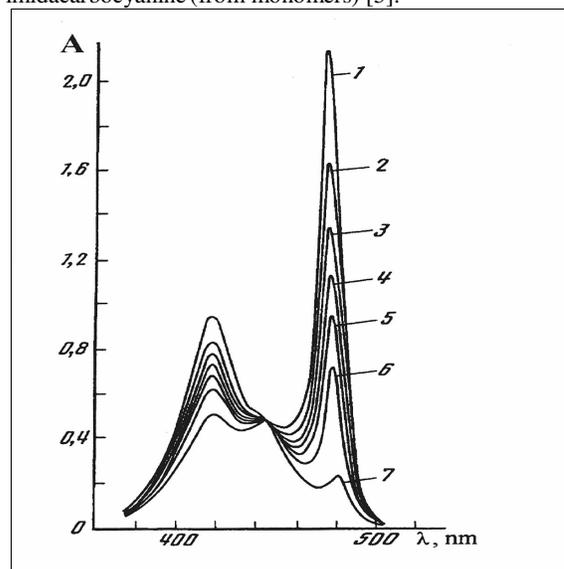


Figure 1. Absorption spectra of dye-1 ($C=10^{-5}M$) in water at $t=10$ (1), 20 (2), 23 (3), 25 (4), 28 (5), 30 (6) and $37^{\circ}C$ (7)

The similar results were obtained for thia-tri- (pyridinium salt of 3,3'-di-(γ -sulfo-propyl)-4,5,4',5'-dibenzo-9-ethylthiacarbocyanine, dye-2) and thiapentamethinecyanine (triethylammonium salt of 3,3'-di-(γ -sulfo-propyl)-9,11-(β,β -dimethyltrimethylene)-10-methylthiapentamethinecyanine, dye-3) [7]. On the Fig. 2 an equilibrium between dimers (D) and J-aggregates of thiapentamethinecyanine dye-3 is shown. The equilibrium is thermodynamic reversible and spectral curves pass through isobestic point. For dye-2 and dye-3 $m=2$, that is, the J-aggregates consists from two dimers or four monomer molecules too.

The study of an equilibrium between the various forms of anionic cyanine dyes in water solutions has allowed to make paradoxical, on the first sight, conclusion, that a method of "block building" of J-aggregates from dimers are the most preferable for construction of "ideal" J-aggregates of the same size (monostructural J-aggregates) [7].

Formation of molecular ensembles

Use of the method of the "block building" of J-aggregates has allowed to receive the mixed J-aggregates from cyanine dyes with a various length of the polymethine chain. The adopted scheme includes: (i) a preliminary stage of dimerization by shifting the J-D-equilibrium toward dimers (upon heating) and (ii) the formation of mixed aggregates (upon cooling).

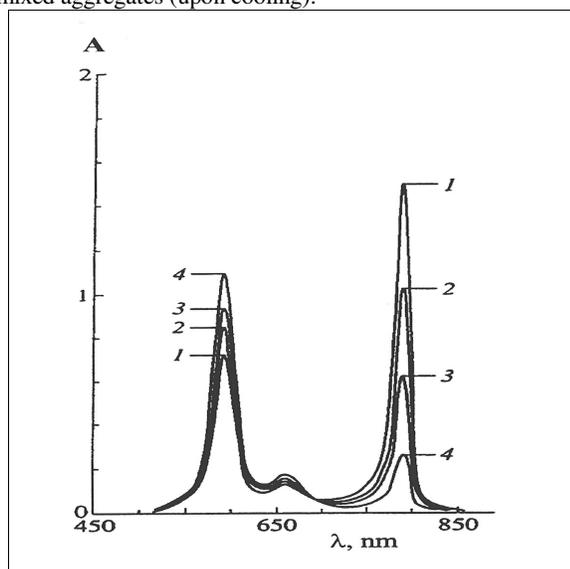


Figure 2. Absorption spectra of dye-3 ($C=5.2 \times 10^{-6} M$) in water at $t=22$ (1), 26 (2), 29 (3) and $32^{\circ}C$ (4)

It is shown for composition of thiatrimethinecyanine (dye-2) and thiapentamethinecyanine (dye-3). The absorption spectra of dye-2+dye-3 mixed solutions represent a superposition of the spectra of individual dyes (Fig.3, curve 1). Upon heating to 50–80°C, the J-aggregates of individual dyes decompose, which gives rise to the absorption bands of dimers (Fig.3, curve 2). Upon subsequent cooling, dimers form new kinds of J-aggregate that contain different dye molecules (Fig.4, curve 3). The absorption of mixed J-aggregates manifests itself at longer wavelengths compared to the J-aggregates of dye-2 but at shorter wavelengths compared to the J-aggregates of dye-3 (790 nm). Process of formation of the mixed J-aggregates is thermodynamic reversible like in the case of the individual dyes.

The described phenomenon has the general character for polymethinecyanines capable to form J-aggregates in water solutions and having highly developed π -conjugated system in heterocycles. Bathochromic shift of absorption bands peaks of the mixed J-aggregates of thiatrimethine- and thiapentamethinecyanines relative to band of J-aggregates of thiatrimethinecyanines is defined by a structure of the last and makes 55-98 nm. Thus, it is possible to receive the mixed aggregates with the desired spectral properties by selection of the pairs of dyes.

As may be concluded from the fluorescence spectra [7], mixed J-aggregates represent homogeneous structures that remind solid

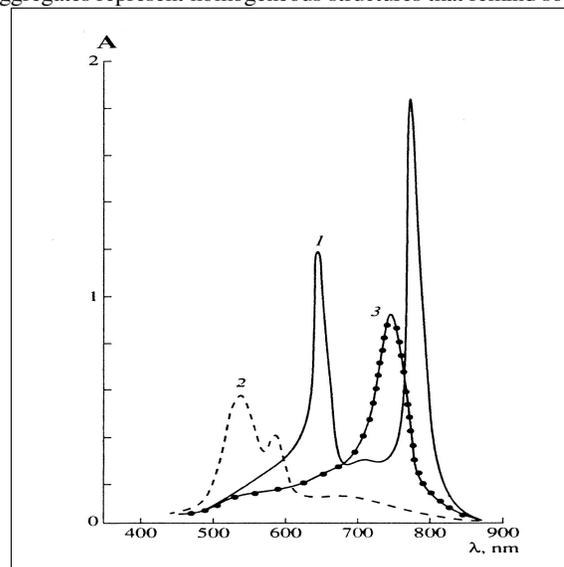


Figure 3. Absorption spectra of the 1 : 1 mixtures of aqueous solutions ($C = 10^{-4} M$) of dye-1 and dye-3: just after mixing at $20^{\circ}C$ (1), upon heating up to $50^{\circ}C$ (2) and upon cooling down to room temperature (3)

solution of dyes. As follows from spectra, instead of bands of luminescence of individual dyes (712 and 822 nm) the new band with $\lambda_{max} = 788$ nm is observed.

Essential and basic difference of the received by the author results from earlier published ones [9] is a finding of a new method of preparation of the mixed J-aggregates of cyanine dyes from dimers in the homogeneous environment instead of on an interface of two phases. Thus, the considered method of "block building" of J-aggregates in a solution appears as a rather effective way of preparation of J-aggregates as well as the mixed J-aggregates from cyanine dyes with various length of polymethine chain. It opens a way for formation of the complex organized structures - molecular ensembles with new electronic, optical and photographic properties.

Other type of aggregates from dimers of various cyanine dyes was received at research of the dyes considerably distinguished in the length of a polymethine chain - thiamonomethinecyanines and thiapentamethinecyanines (dyes of structure I, $N=0$ and $N=2$, respectively). Formation of the mixed J-aggregates in this case was not observed. The absorption bands of dimers of thiapentamethinecyanines were disappeared and the new absorption bands were formed. It is shown in the Fig.4 where absorption spectra of water solutions of triethylammonium salt of 3,3'-di-(γ -sulfopropyl)-4,5-benzo-5'-Cl-thiamonomethinecyanine (dye-1) and triethylammonium salt of 3,3'-di-(γ -sulfopropyl)-9,11-(β,β -dimethyltrimethylene)-10-methyl-thiapentamethinecyanine (dye-4) are shown. Thiamonomethinecyanine is in dimer ($\lambda_{max}=421$ nm) and monomer ($\lambda_{max}=442$ nm) forms (Fig.4, curve 1). The monomer form is expressed as a shoulder on a long-wave branch of an absorption band of dimers. Thiapentamethinecyanine is also in dimer ($\lambda_{max}=588$ nm) and monomer ($\lambda_{max}=655$ nm) forms (Fig. 4, curve 2). Curve 3 on the Fig. 4 characterizes an absorption spectrum of mixed equimolar solutions of dye-1+dye-4. At mixing of dye solutions significant reduction of intensity of

dimer band of thiapentamethine cyanine and occurrence of new absorption bands with $\lambda_{\max}=444$ nm and $\lambda_{\max}=678$ nm are observed. It is shown by a curve 4 received by subtraction of curves 1 and 2 from curve 3 Fig.4. Similar interaction of thiamonomethinecyanines and thiapentamethinecyanines has the general character without dependence on substitutes in heterocyclic rings of dyes. It is worthy of note that when thiapentamethinecyanine dye-3 formed J-aggregates together with dimers, reduction of intensity of absorption not only dimer band but also J-aggregate band was observed, apparently due to displacement of equilibrium $dimer \leftrightarrow J\text{-aggregate}$ in the dimer direction.

The discovered aggregates of a new type from dimers of cyanine dyes of a various structure are designated as "heterocontact dimers" [10]. It was assumed that they arise due to $dimer_1\text{-}dimer_2$ interaction of various dyes. Apparently the splitting of dimer band of long-wave dye is connected to splitting of electronic levels of dimer in "heterocontact dimer" as a result of perturbing action of dimer of short-wave dye. It was concluded that the process of formation of "heterocontact" aggregates is more favourable energetically than formation of dimers and J-aggregates of individual dyes. Thus, in this case also the basic building elements of the organized multimolecular structure are dimers.

Conclusion

Summarizing, it is reasonably safe to suggest, that the question is about a new principle of construction of the complex organized systems not from separate "bricks" – molecules but from blocks – dimers, which are the primary organized formations. It is possible that the "block" principle of construction act also in more complex biological structures, i.e. in a live nature.

J-aggregates, as well as heterocontact structures from dyes with various optical and electronic properties are of interest for subnanotechnology, in spectral sensitization of AgHal, in optical transformations in optoelectronics, as molecular base for "optical" computers. Moreover, individual and heterocontact J-aggregates of the small sizes are promising in use in electroluminescent devices and for non-linear optical transformations.

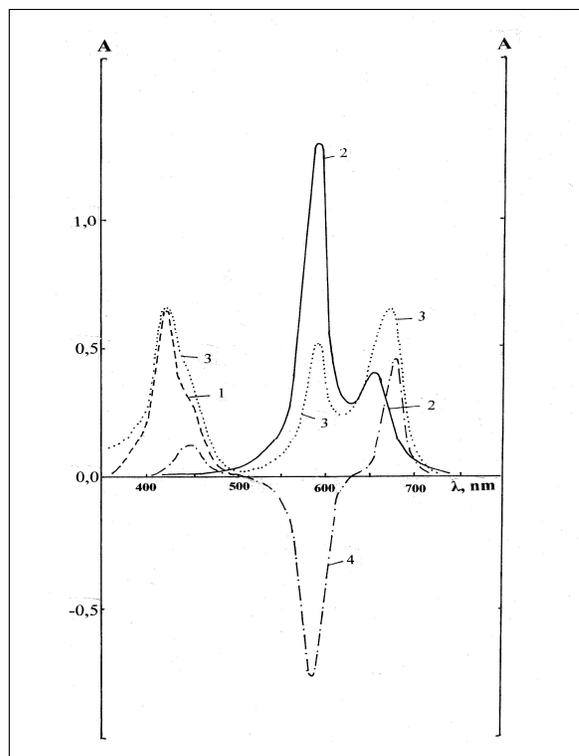


Figure 4. Absorption spectra of water solutions of dye-1 (1), dye-4 (2) and mixtures of dye-1 + dye-4 (3). Concentration of dyes $C=1,0 \times 10^{-5}$ M. Dashed line (4) shows distinction of spectra of initial dyes and their mixed solutions

Acknowledgements

The author would like to thank Dr. V.I.Avdeeva (Scientific Center NIIKHIMFOTOPROEKT) and Prof. A.I.Tolmachev, Dr.Yu.L.Slominsky (Institute of Organic Chemistry, Ukrainian National Academy of Science) for their help in the work and discussion of the results.

This work was supported by RFBR (grant No.04-03-32009).

References

- [1] B.I. Shapiro, The Theoretical Principles of the Photographic Process (Editorial URSS, Moscow, 2000).
- [2] E.I. Mal'tsev, D.A. Lypenko, B.I. Shapiro et al., Appl. Phys. Lett., **17**, 1896 (1999).
- [3] A.V. Vannikov, A.D. Grishina, B.I. Shapiro et al., Chem. Phys., **287**, 261 (2003).
- [4] S. Daehne, S.Kulpe, Structural Principles of Unsaturated Organic Compounds (Akademie Verlag, Berlin, (1977).
- [5] A.H. Herz, Photogr. Sci. Engineering., **18**, 323 (1974).
- [6] T.H. James, The Theory of Photographic Process, 4-th Ed. (McMillan Publ., NY, London, 1977).
- [7] V.I. Avdeeva, B.I. Shapiro, Sci. Appl.Photo., **42**, 511 (2001).
- [8] V.I. Avdeeva, B.I. Shapiro, Sci. Appl. Photo., **41**, 129 (1999).
- [9] Y. Yonezawa, T. Miyama, H. Ishizawa, J.Imag. Sci. Technol., **39**, 331 (1995).
- [10] V.A. Avdeeva, Y.G. Semenkina, B.I. Shapiro, High Energy Chem. (in press).

Author Biography

Boris I. Shapiro, Dr. of Sciences, Professor, Head of Laboratory of Physical-Chemical and Photographic Investigations of Scientific Center NIKHIMFOTOPROEKT, Director of the Education Center NIKHIMFOTOPROEKT-Moscow Institute of Fine Chemical Technology. President of Russian Society of Photographic Science and Technology.

State Prize Winner URSS, 1983 . The author more than 350 publications in scientific journals, 1 book and 10 article reviews. The field of scientific interest includes photochemistry, scientific and applied photography, spectral sensitization of photographic materials and optical recording materials.