Spectral study of the aggregation of benzothiazolic cyanine dyes in solutions and polymolecular layers

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The formation of *J*-aggregates of three polymethine dyes in solutions and in Langmuir—Blodgett (LB) polylayers was studied. The dyes form *J*-aggregates in mixtures of solvents of different polarity: hexane—chloroform and heptane—chloroform taken in various ratios. The formation of *J*-aggregates in LB polylayers depends on the type of matrix and on the matrix : dye ratio.

Key words: benzothiazolic dyes, *J*-aggregates.

The preparation of photosensitive films based on benzothiazolic cyanine dyes (BTCD) using Langmuir—Blodgett (LB) technology, which allows one to create ordered layers of a dye—matrix mixture and to vary the concentration of the dye in these layers,[1—3] is of special interest for the creation of systems of multifrequency optical memory on optical disks. This makes it possible to choose the conditions under which the formation of aggregates of a dye is highly probable.

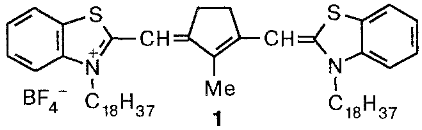
It should be mentioned that there is certain interest in the classes of dyes whose *J*-aggregates have absorption bands coinciding with the irradiation region of small-scale semiconducting lasers (650 to 900 nm). There are several dyes that satisfy these conditions and form *J*-aggregates in solutions and in LB polylayers.[4—6]

The formation of *J*-aggregates in LB polylayers and their photochemical properties depend on the structure of the dye, the type of the matrix, and the microenvironment of the dye in the cage of the matrix.[5] Phospholipids and arachic and stearic acids are used as matrices.[6]

The purpose of this work is to study the formation of *J*-aggregates of three different benzothiazolic cyanine dyes in solutions and in LB polylayers.

Experimental

The following dyes were chosen as the objects of the study:



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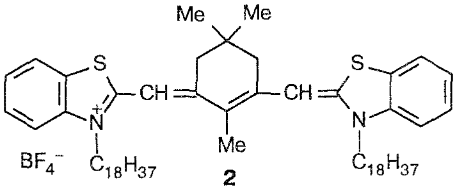

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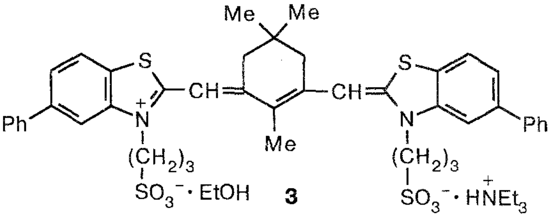

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Polylayers were prepared by the known procedure[7] on a Joyce-Loebl installation (Great Britain). The conditions of the deposition: triply distilled water as the subphase, $CdCl_2$—$NaHCO_3$ as the buffer, pH 6.9; 18 °C, the moisture content in an atmosphere was 45 %. Hexane, heptane, chloroform and chloroform—heptane and chloroform—hexane mixtures in certain ratios were used as solvents.

The irradiation was performed on a LOS-2 installation using interference light filters. Electronic absorption spectra were recorded on UV-Vis 160 and UV-Vis-NIR 3100 instruments (Shimadzu, Japan).

Results and Discussion

π—A-Isotherms (π is the surface pressure in a layer and A is the surface area of a layer) are presented in Fig. 1 for individual dyes and for dye—aliphatic acid mixtures. The π—A-isotherm of dye **1** indicates that two

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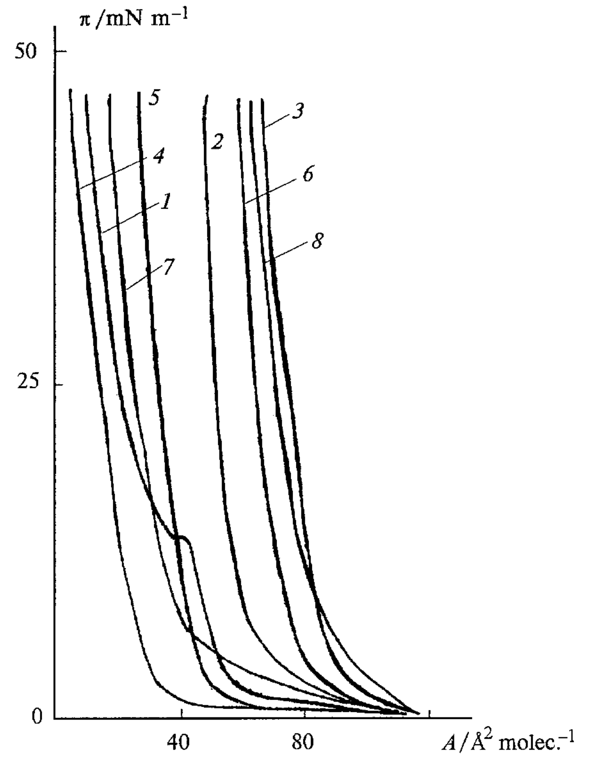

Fig. 1. π—*A*-Isotherms of individual dyes **1**, **2**, and **3** (curves *1*, *4*, and *7*, respectively) and their mixtures with aliphatic acids (curves *2*, *3*, *5*, *6*, and *8*): *2*, PEG 1000—stearic acid—dye **1** (1 : 1 : 2); *3*, dye **1**—stearic acid (1 : 1); *5*, dye **2**—behenic acid (1 : 1); *6*, dye **2**—stearic acid (1 : 1); *8*, dye **3**—stearic acid (1 : 1).

distinctly pronounced phases exist (see Fig. 1, curve *1*). The second phase is explained by the formation of dimers, which comprise monolayers of the dye at the pressure >10 mN m^{-1}. Dyes **2** and **3** form condensed monolayers on the interface (see Fig. 1, curves *4* and *7*, respectively). Despite the introduction of aliphatic substituents with long chains into the structure of the dye, the transportation of monolayers composed of individual dyes is connected with certain difficulties. The transport coefficient decreases in the process of deposition, which affects the change in the optical density (*D*) as the number of monolayers (*n*) increases, because in this case the dependence of *D* on *n* is not linear (Fig. 2). To eliminate this disadvantage, dyes were transported to a solid substrate in a mixture with an aliphatic acid (see Fig. 2, curve *1*).

It should be mentioned that at a surface pressure of 30 mN m^{-1} the monolayers exist in the solid crystalline state, which ensures close packing of the dye in the aliphatic acid matrix and, judging by the nature of the isotherms themselves, the minimum (in the first approximation), in our opinion, imperfection of the structure on the substrate.

Solutions of BTCD. Mixtures of solvents of different polarity were used for the preparation of *J*-aggregates of dyes in solutions. It should be mentioned that dye **1** forms no aggregates under these conditions, and its aggregates were prepared in mixtures of polyethylene glycol (PEG 1000), stearic acid, and **1** (1 : 1 : 2) in chloroform (Fig. 3, curves *1* and *2*). The formation of a *J*-aggregate is accompanied by a 1.3-fold decrease in the optical density of the monomeric form (λ_{max} = 619 nm) in the electronic absorption spectra (see Fig. 3, curve *2*), and the appearance of a new absorption band at 811 nm. Dyes **2** and **3** form aggregates in chloroform—hexane (1 : 7) and heptane—chloroform (1 : 15) mixtures, respectively (see Fig. 3). The introduction of two symmetric phenyl substituents at position 5 of the benzene rings of the benzothiazolic residues in the structure of dye **2** and the replacement of the uncharged hydrophobic $C_{18}H_{37}$-substituents at N atoms by charged *N*-sulfopropyl groups (structure **3**) result in a 52 nm bathochromic shift of the absorption band of the monomeric form (618—670 nm, see Fig. 3, curves *5* and *6*) and a 24 nm hypsochromic shift of the absorption band of the *J*-aggregate at 791 nm (**2**) and 767 nm (**3**).

One can draw the conclusion from the results obtained that these dyes form *J*-aggregates in solutions, and the spectral characteristics of the monomeric and aggregate forms depend on their structures.

The absorption bands of the *J*-aggregates of dyes **1**—**3** coincide with the irradiation region of semiconducting lasers, and therefore it is interesting to study these dyes using LB technology for the preparation of polymolecular layers with the corresponding spectral parameters.

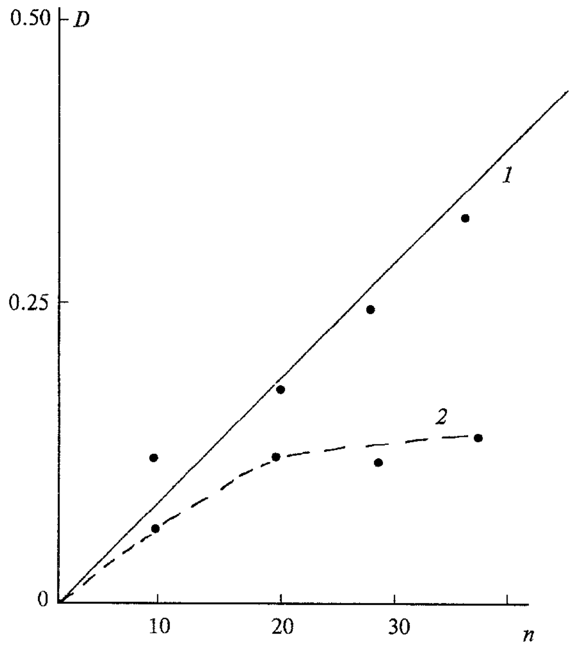

Fig. 2. Dependence of the optical density (*D*) on the number of deposited monolayers (*n*) for the dye—aliphatic acid mixture (*1*) and for the individual dye (*2*).

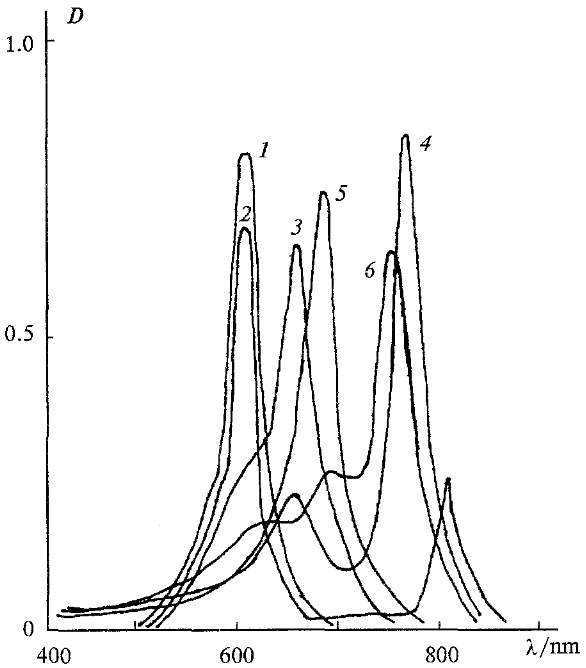

Fig. 3. Electronic absorption spectra of the monomeric forms of dyes **1**, **2**, and **3** (curves *1*, *3*, and *5*, respectively) and of their *J*-aggregates (curves *2*, *4*, and *6*, respectively) in solutions. The conditions for the preparation of aggregates: **1**, the PEG 1000—stearic acid—dye **1** (1 : 1 : 2) mixture in chloroform; **2**, the chloroform—hexane (1 : 7) mixture; **3**, the heptane—chloroform (1 : 15) mixture (the concentration of dyes is 10^{-6} mol L^{-1}).

LB polylayers. Dye—aliphatic acid (1 : 1) mixtures were used for the preparation of LB films. The number of deposited active layers is given in the corresponding figure captions. The maximum of the absorption band in the electronic spectrum of the mixture of dye **1** with stearic acid (Fig. 4) is hypsochromically shifted by 79 nm compared to the spectrum of the solution (619 and 540 nm for the solution and the film, respectively; see Fig. 4, curves *1* and *2*). This shift is caused by the formation of H-type aggregate structures (dimers and trimers). Heating the film at 70 °C for 60 min results in a decrease in the optical density at the absorption maximum (540 nm) and the simultaneous appearance of an absorption band at 630 nm and its increase over time (see Fig. 4, curve *3*). It should be mentioned that this process is characterized by an isobestic point (see Fig. 4), which testifies that there are dimers of the dye in the LB polylayers and they are in equilibrium with its monomeric form. Heating causes the equilibrium to be shifted towards the formation of monomers; after 60 min of heating, the absorption spectrum of the dye takes the shape shown by curve *3*, and further heating at 70 °C does not result in noticeable changes in the absorption spectrum.

The deposition of dye **1** mixed with stearic acid and polyethylene glycol (M = 1000) in layers, which repeats the conditions of the preparation of the aggregate in solution for LB films (*cf.* Fig. 3, curve *2* and Fig. 4, curve *4*), results in an 81 nm bathochromic shift of the absorption band in the electronic spectrum of the dye compared to the spectrum of the solution (see Fig. 4, curves *1* and *4*). This testifies in favor of the formation of *J*-aggregates. The band obtained is strongly broadened, apparently due to the formation of aggregates that differ in size.

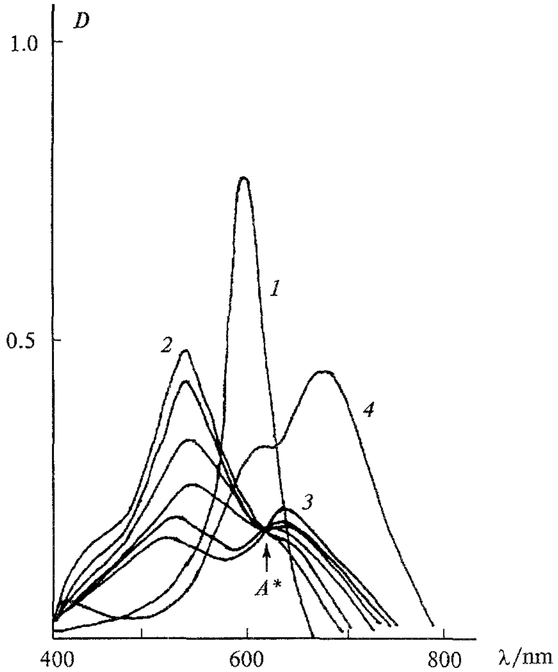

Fig. 4. Electronic absorption spectra of dye **1** in LB polylayers: *1*, the monomeric form in chloroform; *2*, 40 layers of the **1**—stearic acid (1 : 1) mixture; *3*, the **1**—stearic acid film after 60 min of heating at 70 °C (A^* is the isobestic point); *4*, 40 layers of the PEG 1000—stearic acid—**1** (1 : 1 : 2) mixture.

The absorption spectrum of the LB film of dye **2** mixed with stearic acid has a weak bathochromic shift compared to the spectrum of the solution (Fig. 5, curves *1* and *2*) and is the same as the absorption spectrum of the monomeric form of dye **2**. Heating this film results in a decrease in the optical density (see Fig. 5, curve *3*); a similar result is also obtained after irradiation (see Fig. 5, curve *4*), which probably attests to irreversible changes in the dye in the film. When the matrix is displaced, *i.e.*, when dye **2** is deposited in the mixture with behenic acid, there is a bathochromic shift of the absorption band by 50 nm (see Fig. 5, curve *5*), but, like in the case of dye **1**, this band is broadened.

The absorption band of dye **3** in LB polylayers in the mixture with stearic acid is narrow and is characterized by a strong bathochromic shift with respect to the absorption band of the monomeric form in solution (by almost 100 nm; see Fig. 5, curves *6* and *7*). In this case, the *J*-aggregate has a typical absorption spectrum.

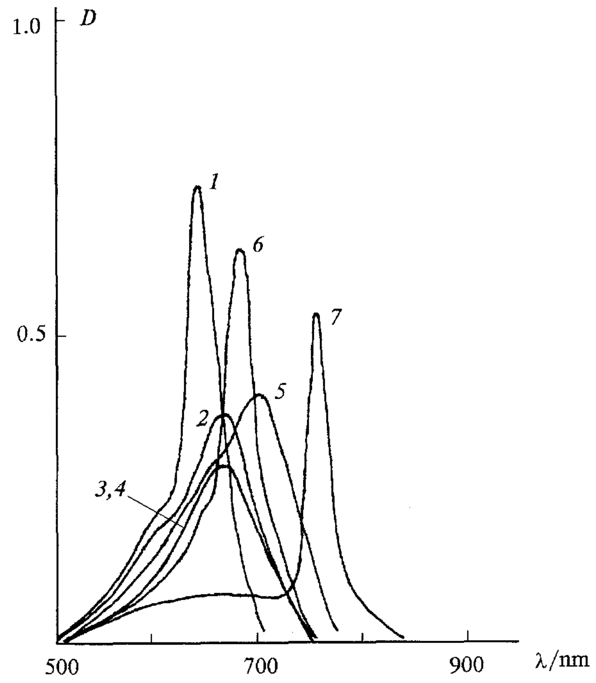

Fig. 5. Electronic absorption spectra of dyes **2** and **3** in LB polylayers: *1* and *6*, the monomeric forms of dyes **2** and **3**, respectively, in chloroform; *2*, 20 layers of the **2**—stearic acid (1 : 1) mixture; *3*, the **2**—stearic acid film heated at 70 °C for 5 min; *4*, the **2**—stearic acid film irradiated at the absorption maximum for 5 min; *5*, 20 layers of the **2**—behenic acid (1 : 1) mixture; *7*, 20 layers of the **3**—stearic acid (1 : 1) mixture.

As can be seen from the results obtained, the matrix in which the dye is incorporated to form LB layers strongly affects the behavior of the dye in the film. Therefore, the correct choice of the matrix (which is tightly associated with the structure of the dye itself) and of the dye : matrix ratio for each given dye is a necessary condition for the formation of aggregates. It is likely that for dyes **1** and **2** the broadening of the absorption spectrum of the *J*-aggregates is caused by the improper choice of the dye : matrix ratio (see Fig. 4, curve *4* and Fig. 5, curve *5*), although the matrix was chosen correctly. Thus, we found the conditions under which all three dyes form *J*-aggregates in solutions and in LB polylayers. The detailed analysis of the π—A-isotherms and the diagrams of the dependence of the surface area per molecule on the composition of the dye : aliphatic acid mixture obtained by the method of monolayers will be presented in our next publications.

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