Solvent-Induced Organization of Squaraine Dyes in Solution Capillary Layers and Adsorbed Films

O. P. Dimitriev,*,† A. P. Dimitriyeva,† A. I. Tolmachev,‡ and V. V. Kurdyukov‡

Institute of Semiconductor Physics, pr. Nauki 45, Kiev 03028, Ukraine, and Institute of Organic Chemistry, Murmanskaya str. 5, Kiev 02094, Ukraine

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Unusual behavior of indolenine and hydroxyphenyl squaraines has been observed in solution capillary layers and adsorbed films. The confined solutions showed anomalous aggregation of squaraine molecules in contrast to their monomer behavior in the bulk solutions of the same concentration, along with formation of a macroscopic cell-like structure in the confined solution layer, with the diameter of cells being 3−5 μm. The aggregate structure, as observed through electronic absorption spectra, was strongly dependent on the chemical structure of squaraine used and solvent used, and it also was different from squaraine aggregates observed in aqueous solutions and films prepared by vacuum evaporation. It has been found that indolenine squaraine is capable of forming H-aggregates in confined dimethylformamide solutions and hydroxyphenyl squaraine is capable of forming J-aggregates in confined dimethylformamide solutions and adsorbed films. The results were compared with pseudoisocyanine, which forms J-aggregates in aqueous bulk solutions readily; however, no J-aggregates have been found in their capillary layers. The interplay of dye−dye, dye−surface, and dye−solvent interactions resulting in the above effects is discussed.

1. Introduction

It is well-known that liquid matter has unusual properties in the confined geometry. These unusual properties are due to a surface-induced long-range order of molecules being near the solid−liquid interface, which leads to formation of the liquid crystalline state for a liquid layer near the surface.[1,2] The addition of molecules with chromophore groups to liquids in the confined geometry serves two purposes. The first one is to monitor structural changes of the liquid layer near the surface using conventional spectroscopic techniques that probe changes in absorption and/or luminescence spectra of the chromophore groups. The second purpose is to monitor the arrangement of the dye molecules themselves, which is the result of dye−dye, dye−solid, and dye−solvent interactions, with the latter occuring in the liquid environment with another structure than that of the bulk liquid.

Recently, we have shown that polymer molecules, namely, polyaniline, undergo conformational changes in thin capillary layers of the dimethylformamide solution.[3,4] The changes are normally associated with the expanded-coil to compact-coil conformational changes and were explained by high adsorption of the polymer molecules at the liquid−solid interface, when the adsorption process creates a concentration gradient along the normal to the surface and forces the polymer molecules to reduce their hydrodynamic volume. To our knowledge, the analogous phenomena for small molecules have not been studied yet.

In this study, we report the behavior of squaraine dyes in confined solutions. Squaraines have been the subject of intense investigations due to their unusual electronic properties which give rise to their use as semiconductive and photogeneration materials in xerographic devices,[5] as sensitizers in photovoltaic devices,[6,7] as films for second-harmonic generation,[8−12] as constituents for oligo- and poly-squaraines with electrical conductivity,[13] as ligands for the sensing of metal ions,[14,15] and so forth.

Squaraines are known to readily associate even in dilute solutions[16] and to be highly surface-active molecules as compared with other well-known 2D molecular systems.[17] They exist as monomers in aqueous solutions of β-cyclodextrin, with the absorption maximum at $\lambda_{max} = 650$ nm.[18] The aggregation behavior of squaraines has been studied in solutions,[19−21] in microheterogeneous media,[22] in Langmuir−Blodgett (LB) films,[23−25] and also in microcrystals.[26,27] The association number in the squaraine aggregate is dependent upon the ring substituents and dialkylamino groups. Condensed films of squaraines are polymorphic and show two limiting cases with respect to the overlap and mutual orientations of chromophores, namely, the H-aggregate phase with a "cardpack" arrangement of the molecules and a sharp absorption maximum at ∼520−530 nm and the J-aggregate phase with a "slipped stack" or 'head-to-tail" arrangement and an absorption maximum at ∼750−770 nm.[22,28] There is also an intermediate case when the absorption band is splitting into two components around the monomer absorption band. That is the Davydov splitting which is related to the "oblique aggregate", when transition dipole moments of neighboring molecules form a certain angle to each other.[29] This case most probably corresponds to the T-shape aggregate structure observed in a stable polymorph of dimethylamino hydroxylated squaraines, in which molecules intersect at 90° through Coulomb interaction between negatively polarized oxygens and positively polarized nitrogens of the adjacent molecules.[17] It has been shown that squaraine aggregates in solutions have a stable form which exhibits the absorption band at ∼530 nm. Such a behavior shows that the H-aggregate arrangement of squaraines is more preferable in solutions. Chen

* Corresponding author.
† Institute of Semiconductor Physics.
‡ Institute of Organic Chemistry.

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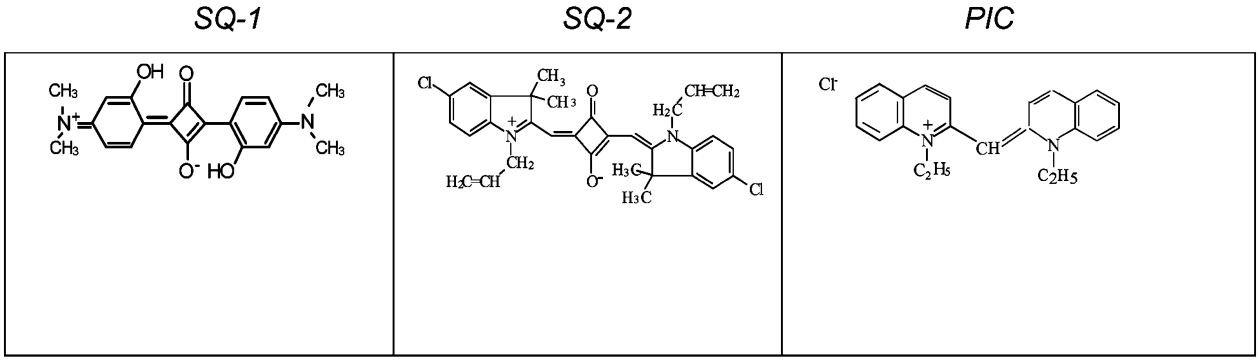

Figure 1. Chemical structures of the dyes used.

et al. have reported that the blue-shifted absorption ($\lambda_{max} = 530$ nm) can be assigned to a cyclic chiral structure of tetrameric aggregates formed.[22,28] In addition to H-aggregation, monolayers at the air−water interface and LB films on solid supports can also realize either an oblique aggregate or J-aggregate arrangement.[28] However, special conditions for that are needed, that is, certain substituent groups and relatively high compression for the formation of LB films. It should be noted that both oblique aggregates and J-aggregates are metastable in pure monolayers and can be readily rearranged to H-aggregates.

On the other hand, it is known that various cyanine, merocyanine, indocyanine, and so forth, dyes readily form stable J-aggregates in solutions, in the adsorbed layer at the solid−liquid interface, and in organized monolayers at the liquid−air interface.[30−33] To form a J-aggregate, the dye structure has to meet certain geometrical requirements. Typical compounds forming J-aggregates have the transition dipole moments along the long molecular axis and substituents which force the molecule to pack in a head-to-tail, "brickstone", or "herringbone" fashion.[34,35] In principle, squaraines conform to such a requirement. However, the formation of the squaraine J-aggregate in a bulk solution has not been observed yet. J-aggregation of squaraine dyes with short alkyl chains[36] and long alkyl chains[37] has been observed in thin Langmuir−Blodgett films. The J-aggregate phase of squaraines is also possible in their crystalline bulky films.[22,23]

In this study, we report an observation of J- and H-aggregation of squaraines in confined solutions of a capillary thickness. We compare, on one hand, the behavior of different squaraines (Figure 1) which do not form J-aggregates in the bulk solution and, on the other hand, the behavior of pseudoisocyanine (PIC) dye which readily forms J-aggregates in the bulk aqueous solution.

2. Experimental Section

The synthesis of the dyes has been described elsewhere.[38] Two types of squaraine (SQ) dyes were used in this study. The first dye was dimethylamino hydroxyphenyl squaraine (SQ-1), and the second dye was a derivative of indolenine squaraine (SQ-2) (Figure 1). The main difference between these dyes is that the SQ-1 has a rigid flat structure, which may be additionally stabilized by the formation of intramolecular hydrogen bonding, while SQ-2 contains bulky indolenine groups which can rotate around the molecular axis in solutions.

The dyes have been dissolved in either dimethylformamide (DMF) or chloroform, with the concentration being no more than 10^{-4} M. The solutions were embedded into quartz cells with a thickness of 1 mm, which from here on will be referred to as bulk solutions, and into capillary cells, which will be referred to as confined solutions. Microscope glass substrates served as a material for capillary cells. The confined solutions were prepared by depositing a solution drop of the given volume onto a glass surface and then covering it with the same plate, so that the gap between two plates was filled by the solution completely. The thickness of the confined solutions was calculated using the data on the solution volume and area of the plates wetted with the solution, and the determined gap value was in the range from 10 to 30 μm. Adsorbed films were prepared on glass substrates by immersing a microscope glass plate into the dye solution for several hours.

Electronic absorption spectra of the samples were recorded using a SPECORD M-40 dual-beam spectrophotometer. The cell with a pure solvent confined by two bare plates served as a reference. The light beam was set perpendicular to the sample surfaces. Microscopy studies have been performed using an Axiostar Plus microscope (Carl Zeiss) equipped with a photocamera and a computer.

3. Results

3.1. Electronic Absorption Spectra of Squaraines: General Behavior. *(a) Solutions.* The electronic absorption spectra of both SQ-1 and SQ-2 dyes in diluted DMF solutions were almost identical. The spectra showed a single absorption band in the visible with a maximum at ∼645 nm, typical of the monomer absorption (Figure 2). The identity of absorption spectra of SQ-1 and SQ-2 means that the end groups of the molecule do not affect the basicity of the chromophore.[39,40] To induce molecular aggregation, a binary solvent mixture has been used, one component of which, that is, DMF, dissolves SQ molecules well, while the other, namely, water, does not, whereas the both liquids are mixing well. Figure 2 shows electronic spectra of SQ-1 and SQ-2 in the binary mixture of DMF/water with a solvent volume ratio of 1:100. The spectra of the dyes in DMF/water solutions become transformed as compared with their monomer spectra in the diluted DMF solution. The changes are different depending on the SQ structure. The spectrum of SQ-2 shows relatively high broadening, with the absorption maximum being at ∼640 nm, which is only slightly shifted with respect to the monomer absorption maximum. Such a behavior points out that the chromophore groups of SQ-2 do not overlap in a well-ordered manner, probably due to the bulky end groups of SQ-2 molecules which can twist out of the chromophore plane. On the other hand, the spectrum of SQ-1 shows a significant shift to shorter wavelengths, with the maximum being at ∼543 nm. Such a spectral shift corresponds to the formation of H-aggregates.[22,23]

(b) Thin Films Deposited in a Vacuum. To give more details of how different squaraines can aggregate, we present here results on vacuum-deposited films which have been described in detail in our previous work.[41] The aggregation of SQs can

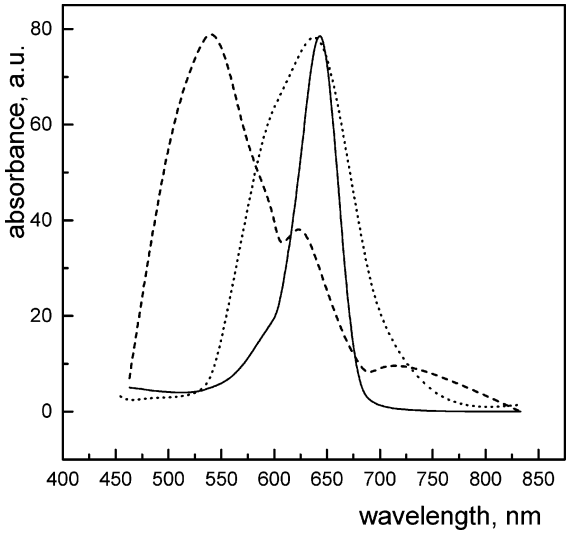

Figure 2. Electronic spectra of diluted bulk DMF solutions of SQ-1 and SQ-2 (solid line), bulk water/DMF solution of SQ-1 (dashed line), and bulk water/DMF solution of SQ-2 (dotted line). The concentration of the solutions are $\sim 3 \times 10^{-6}$, $\sim 3 \times 10^{-8}$, and $\sim 7 \times 10^{-7}$ M, respectively, and the ratio of DMF to water is 1:100. All the spectra are normalized to the same maximum.

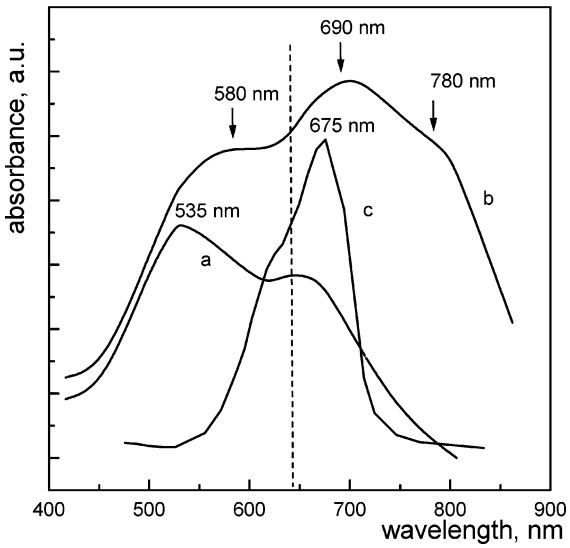

Figure 3. Comparison of electronic absorption spectra of SQ films deposited in a vacuum: (a) thin SQ-1 film; (b) thick SQ-1 film; (c) SQ-2 film. The dashed line indicates the monomer absorption wavelength.

be monitored at the early stage of their nucleation at the vacuum−solid interface. Vacuum deposition allows a very thin layer to be grown; however, this layer is still different from that obtained by adsorption at the liquid−solid interface because in the former case film growth is a result of dye−dye and dye−solid interactions only, while in the latter case dye−solvent interactions can additionally affect the aggregate structure. It has been found that SQ-1 molecules aggregate at the very early stage of the film formation in a vacuum, since the absorption maximum of a thin film was blue-shifted as compared with the monomer absorption (Figure 3a). Therefore, one can conclude that dye nucleation and formation of H-aggregates of SQ-1 is favorable even at the early stage of vacuum deposition, when the concentration of the molecules on the dry surface is very small.

(c) Thick Films. Further influx of the material in the process of vacuum deposition results in the formation of bulky aggregates or crystallites. Electronic absorption in this case is affected by molecular packing and intermolecular interactions, respectively, which is different for SQ-1 and SQ-2 due to the different end groups attached to the squaraine chromophore. For comparison, we show spectra of films of SQ-1 and SQ-2 evaporated in a vacuum under similar conditions (Figure 3b,c). The spectrum of the SQ-2 film shows only band broadening and a slight shift of the absorption maximum with respect to the monomer band, and the absorption profile is almost unchanged with film thickness. Thus, spectral changes of SQ-2 films are similar to those observed for SQ-2 aggregates in solutions. Therefore, one can suggest similar aggregate structures of SQ-2 in films and in solutions. The spectrum of the thick SQ-1 films, however, is strongly different from that of aggregates in solutions and thin films. It shows strong broadening and splitting of the absorption band into three components at least. Therefore, one can conclude that the aggregate structure of SQ-1 should be transformed as the film thickness increases, due to the change/appearance of crystalline polymorphs in the growing film. The spectral changes can be assigned to the appearance of two new polymorphs in thick SQ-1 films, which correspond to oblique aggregates yielding a splitting band with components at 580 and 690 nm (Figure 3b) and J-aggregates with the absorption band at ~780 nm.[22,28] Such a behavior is quite consistent with the coexistence of various polymorphs in the condensed SQ films.[6,42]

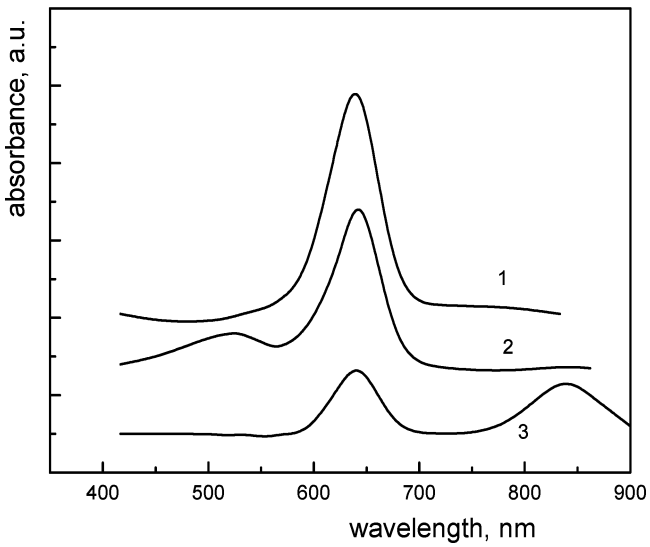

Figure 4. Absorption profiles of capillary layers of (1) both squaraines in chloroform, (2) SQ-2 in DMF, and (3) SQ-1 in DMF. The concentration of the SQ-1 solution is $\sim 3 \times 10^{-6}$ M, and the concentration of the SQ-2 solution is $\sim 7 \times 10^{-6}$ M.

3.2. Behavior of Squaraines in Confined Solutions and Adsorbed Films. *(a) Solutions.* Capillary solutions showed changed electronic absorption spectra as compared to the absorption spectra of the bulk solutions of the same concentration. The changes were strongly affected by the solvent used and the dye structure. Chloroform resulted in only a modest change in the spectra for both squaraines, that is, broadening of the absorption band (the full width at half-maximum (fwhm) was ~1.5 times higher as compared with that of the monomer band in the bulk solution) without spectral shift of the maximum (Figure 4). Such a behavior points out that some aggregation of SQ-1 and SQ-2 in the capillary chloroform solution occurs, whose molecules are coupled via weak dipole−dipole interactions. The driving force for the aggregation in a capillary solution layer is a tendency for adsorption at the liquid−solid interface, which creates increased molecular concentration near

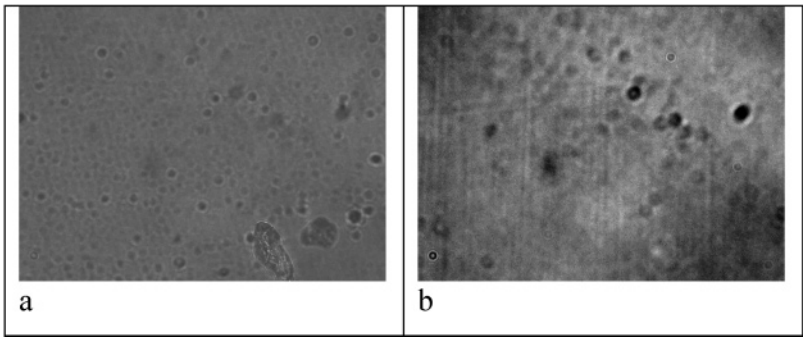

Figure 5. Microscopy images of confined DMF solutions of (a) SQ-1 and (b) SQ-2. The dimensions of the images are 165 × 120 μm^2 each. Glass defects in the lower right corner of the left image can be seen.

the surface and therefore provides the condition for molecular aggregation which causes changes in electronic absorption spectra, as was shown earlier.[3] This conclusion is especially applicable to squaraines which are known to be highly surface-active molecules.[17]

On the other hand, DMF induced significant changes in the spectra of the capillary layers of both squaraines. Besides the conventional broadening of the monomer absorption band, the appearance of an additional band in the visible has been revealed. In the case of SQ-1, this additional band was red-shifted with respect to the monomer absorption, while, in the case of SQ-2, the additional band was blue-shifted (Figure 4). The above changes show that, in addition to the formation of aggregates coupled via weak van der Waals forces, the aggregates with the higher overlap of their chromophores appear in the confined solution of DMF, however with different aggregate structures for SQ-1 and SQ-2, respectively. The aggregate structure of SQ-2 should be similar to the aggregate structure of SQ-1 found in aqueous solutions or thin films deposited in a vacuum because a similar blue shift of the band to ~530 nm occurs in these cases. The above spectral changes correspond to the formation of a cardpack arrangement or H-aggregates.[28] It should be noted that a specific condition to induce H-aggregation of SQ-2 is needed because no H-aggregate has been found in SQ-2 films and aqueous solutions. Such a condition will be discussed later.

In the case of SQ-1, the appearance of an additional band at 780 nm indicates a slipped stack arrangement or J-aggregation with overlap of the neighboring donor and acceptor groups.[28,43,44] It was found, however, that J-aggregates of SQ-1 are unstable because these exhibit an irreproducible intensity and position of the absorption band, the maximum of which is varied in the range ~760−850 nm. Again, specific conditions are needed to induce such an aggregation because no J-aggregate was found in aqueous solutions and thin films deposited in a vacuum.

Microscopy studies of the confined solutions revealed that DMF solutions of both SQ-1 and SQ-2 are not homogeneous. Instead, a self-organized, cell-like structure is formed in the confined layers. The diameter of the cells in the confined SQ-1 solution was ~3−4 μm (Figure 5a). In the case of the confined SQ-2 solution, the formation of a cell-like structure was also observed, with a cell size of ~5 μm (Figure 5b). The driving forces yielding such a structure are not known to us; however, we assume that the borders of the cells are formed by aggregates of the squaraine molecules because such borders should be constructed with something other than liquid molecules.

(b) Films. The appearance of the pronounced band attributable to J-aggregates can also be clearly seen in ultrathin films of SQ-1 prepared by adsorption of the dye molecules from a solution or by film casting. In films obtained by adsorption from a diluted DMF solution, we observed a relatively narrow and intensive band as compared with the rest of the spectrum (Figure 6a). The absorption maximum of this band was at 758 nm, and its fwhm was ~40 nm. A film prepared from more concentrated chloroform solution by casting revealed broadening of this band, probably due to varying structure of these aggregates, along with clear evidence of aggregates of another type indicated by a smeared band at ~595 nm (Figure 6b). It should be noted that the nucleation of J-aggregates from a solution is quite different from their formation in a vacuum, where the J-aggregate phase appears only as a result of structural transformations in a relatively thick film. Again, the role of solvent in the above process should be significant.

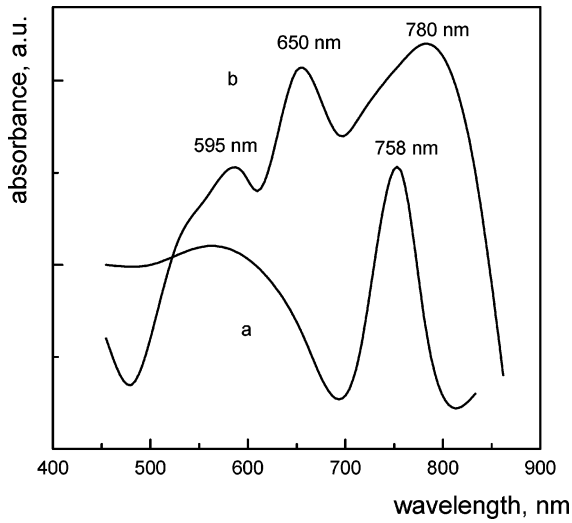

Figure 6. Absorption profiles of ultrathin films of SQ-1 (a) adsorbed from DMF solution and (b) cast from the chloroform solution.

Microscopy studies of SQ-1 films revealed inhomogeneous film structure, with the dye molecules collected into different domains. We have distinguished three regions of the film formation (Figure 7 a):

(1) The region of dye association yielding a bluish color. A more detailed inspection of this region allows us to distinguish the presence of elongated wormlike rows or meanders, which form larger domains observable in Figure 7a as regions extended from the upper left corner to the lower right one. It seems that the intensive J-aggregate band in the spectra originates just from this region because most of the film area belongs to this region.

(2) The region of accumulation of the above associates into a more dense structure which forms a border of the rounded domains with dimensions of ~2−3 μm, which are grouped together on the substrate surface. The origin of these domains is unclear. A clear difference can be seen between the domain border and the domain core. The domain border is as thick as

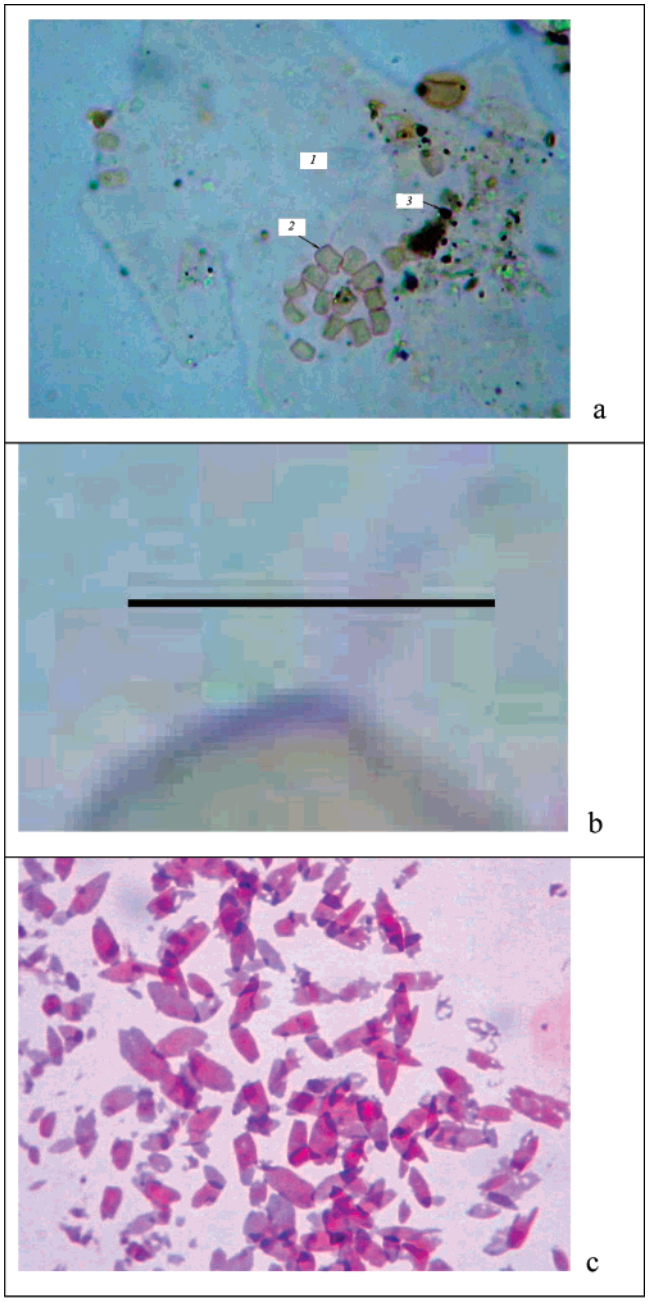

Figure 7. Microscopy images of (a) SQ-1 film adsorbed from DMF solution, (b) magnification of the region near the domain border (the bar length is 2.4 μm), and (c) PIC film cast from DMF solution. The dimensions of images a and c are 66 × 48 μm^2 each.

~200 nm and has a reddish color as observed through the microscope (Figure 7b), whereas the domain core has a yellowish color. It appears that the domains originate from the cell-like arrangement of the dye aggregates in their confined solutions because the size of the domains is comparable with that of the cells (Figures 5a and 7a).

(3)The region of dye nucleation leading to the crystal formation. Such a region has a violet color typical of that of thick polycrystalline SQ-1 films.

It should be noted that the morphology of the adsorbed film of SQ-1 is quite different from that of the vacuum-evaporated film. The latter shows preferable arrangement of the molecules into grains with dimensions of 40−100 nm even in thin films.[41]

3.3. Behavior of Pseudoisocyanine in the Confined Geometry. To compare how various dyes form J-aggregates in the confined solution, we investigated the ability of PIC to form J-aggregates in a capillary solution layer. As known, PIC readily forms J-aggregates in aqueous bulk solutions.[30] The addition of water to a DMF solution of PIC results in suppression of the monomer band at 527 nm and the appearance of a narrow red-shifted band at 581 nm attributable to J-aggregates (Figure 8). The same spectral changes can be found in PIC films obtained, for example, by casting from the DMF solution (spectrum not shown). Microscopy studies revealed the formation of oblong domains in PIC films (Figure 7c). In contrast to the domains of SQ-1 films discussed above, the interiors of the PIC domains are filled homogeneously, pointing out that the domains are microcrystals consisting of the J-aggregate phase. These results show that the PIC molecules prefer to form J-aggregates both in aqueous solutions and in the condensed film.

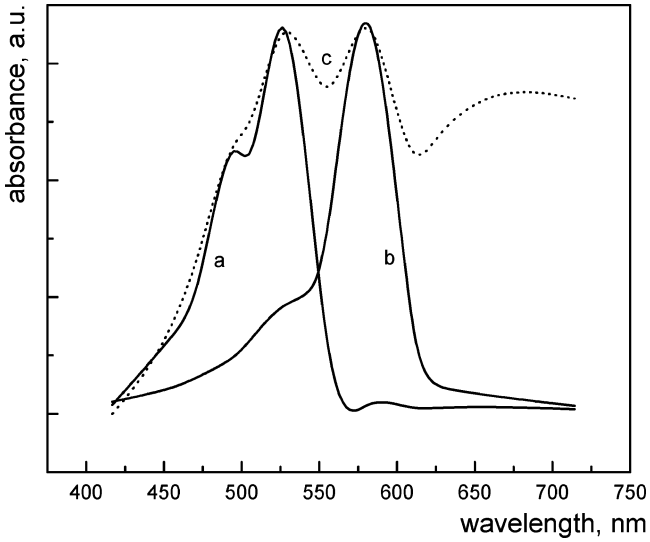

Figure 8. Electronic spectra of (a) PIC in the bulk DMF solution, (b) PIC in the bulk water/DMF solution, and (c) PIC in the confined water/DMF solution. All the spectra are normalized to the same maximum; the concentration of PIC is 5 × 10^{-5} M for all the solutions.

However, a distinct behavior of PIC molecules has been found in their confined solutions. Reduction of the thickness of the aqueous solution of PIC to the capillary layer resulted in suppression of the J-aggregate band (Figure 8). In some cases, this band disappeared completely. Simultaneously with the suppression of the J-aggregate band, the appearance of an additional band at 530 nm was found. This band is highly broadened as compared to the monomer one, so one can conclude on the formation of other aggregates than J-aggregates. It is interesting that J-aggregates of PIC cannot be formed in confined DMF solutions also. These results indicate that the J-aggregate structure of PIC is unfavorable in their confined solutions.

4. Discussion

The above results show that there are three important factors that influence the aggregate structure of the dyes used, namely, the chemical structure of the dye itself, the nature of the solvent used, and the presence of a solid support. The interplay of these factors leads to competition of dye−dye, dye−solvent, and dye−substrate interactions and determines the final aggregate structure. In the case of squaraines, the presence of a solid substrate is essential because these are highly surface-active molecules. SQ molecules in adsorbed films showed the extended region of their distribution (region 1 in Figure 7). Such a distribution points out the high dye−solid interaction, that is, adsorption at

the surface instead of collecting into bulk crystallites. Therefore, adsorption at the liquid−solid interface can be considered as the initial driving force resulting in unusual aggregation. It is known that squaraines not only are highly surface-active but also aggregate well.[17,22,28,43] Thus, adsorption at the liquid−solid interface can be considered as the first step of their complex behavior in the confined solutions. A liquid environment renders the aggregates highly mobile at the surface, so these can migrate to each other, thus forming more compact and complex structures. That is why their structure is different from that of vacuum-evaporated films. Stacking occurs more easily for planar molecules, so a planar structure of dye molecules is essential for their ability to form H-aggregates. That is consistent with the fact that the SQ-1 molecules readily form H-aggregates in the aqueous bulk solution. On the other hand, the absence of H-aggregates of SQ-2 in the aqueous bulk solution is consistent with the probability of their indolenine groups to twist out of the molecular plane, thus causing nonplanarity. A nonplanar conformation of indolenine squaraines was reported even for their crystal structure,[45] so it is expected that the rotation of indolenine groups is highly possible in the liquid environment. Adsorption and aggregation of SQ-2 molecules at the liquid−solid interface suppresses the rotation of the end groups and stabilizes the planar molecular structure which is preferable for the majority of indolenine squaraines in crystals.[46] The surface-induced stabilization of the planar molecular conformation seems to be a reason for the H-aggregate formation of SQ-2 at the solid−liquid interface.

The orientation of the molecules with respect to the surface is also important for their aggregate structure. It has been reported that amphiphilic SQs form either H- or J-aggregates when their long molecular axes are oriented perpendicular to or along the air−water interface, respectively.[28] The parallel-to-the-interface orientation allows for the adjacent molecules in the aggregate to shift along the molecular axis, so that the J-aggregate structure can be formed, whereas no such shift is possible for the perpendicular orientation of molecules to the interface. Thus, one can suggest different orientations of SQ-1 and SQ-2 with respect to the solid support due to their different end groups, namely, the parallel orientation of SQ-1 and the perpendicular orientation of SQ-2 with respect to the surface. The role of solvent is also significant in this process. DMF is a polar solvent possessing a relatively high dipole moment, so it takes part in the ordering of also polar dye molecules at the surface. An independent arrangement of solvent molecules at the liquid−solid interface should also be taken into account. It is known that such an arrangement takes place which is different from the bulk solution, and it undoubtedly can affect the arrangement of dye molecules themselves. Derjagin et al.[1] have concluded that various polar liquids form a liquid crystalline layer near the surface, and this layer can be as thick as ∼100 nm. Thus, dye molecules which tend to adsorb at the surface fall into a liquid crystalline matrix, so that their aggregate formation should conform to the ordered structure of the liquid layer near the surface. We do not have direct evidence that DMF forms an ordered structure near the surface; however, the cell-like arrangement of the confined DMF solutions (Figure 5) indicates in favor of such an assumption. Therefore, we suggest that the ordered DMF molecules near the surface influence the structure of the SQ aggregates formed.

As to PIC, it should be noted that the molecule consists of a positively charged chromophore and a negatively charged counterion. The latter is highly mobile and takes part in the formation of a neutral J-aggregate in the bulk aqueous solution. Adsorption of the PIC molecule at the liquid−solid interface seems to disturb the balance between the chromophore and counterion interactions, and that can be the reason of destruction of the PIC J-aggregates near the surface.

5. Conclusions

Unusual aggregation behavior of different dyes in the confined solution geometry was found to occur as a result of dye−dye, dye−solvent, and dye−substrate interactions. It has been proposed that the initial driving force for the aggregation is high adsorption of dye molecules at the liquid−solid interface, which results in redistribution of the dye concentration across the solution layer, with a higher concentration at the interface. The structure of dye aggregates formed at the liquid−solid interface is suggested to be further influenced by the polarity of the solvent used, orientation of the molecule with respect to the surface, and charge bearing by the chromophore. A high mobility of molecules in the liquid environment causes their different aggregate structures as compared with aggregates formed in a vacuum. As a result, the formation of J- and H-aggregates at the solid−liquid interface is possible for squaraines with different end groups, and the destruction of J-aggregates at the liquid−solid interface has been observed for pseudoisocyanine.

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