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Effects of surfactants on the molecular aggregation of squaraine dye Sq–2Me in aqueous solutions

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The influence of anionic surfactant, sodium dodecyl sulphate (SDS), and cationic one, cetylpyridinium bromide (CPB), on aggregation behavior of squaraine dye Sq–2Me has been studied in aqueous solutions by optical spectroscopy. It has been found that the addition of surfactants at concentrations higher than critical micelle one сщтсутекфешщт into a DMF-W (95 %) solution does not prevent the dye aggregation. The structure of Sq–2Me aggregates formed in SDS and CPB micelles is discussed using the exciton theory. The results show that the optical properties and the Sq–2Me aggregate structure can be tuned using interaction with surfactant micelles of different nature.

В водных растворах методами оптической спектроскопии изучено влияние анионного (додецилсульфат натрия, SDS) и катионного (цетилпиридиний бромид, CPB) поверхностно-активных веществ (ПАВ) на агрегацию скваранового красителя Sq–2Me. Обнаружено, что добавление в бинарный раствор ДМФ-В (95 %) ПАВ в концентрации выше критической концентрации мицеллообразования не препятствует агрегации красителя. Структура агрегатов красителя Sq–2Me, образованных в мицеллах SDS и CPB, рассматривается в рамках экситонной теории. Полученные результаты позволяют сделать вывод о возможности управления структурой агрегатов Sq–2Me при помощи ПАВ разной химической природы.

Functional dyes, π-conjugated molecules and chromophore based systems with new or improved properties attract growing attention, because those can form integral parts of modern electronic and photonic devices [1]. Functional dyes are extremely important in photon based technologies for optical data storage and communications [1, 2]. Squaraines are a class of cyanine dyes being under intensive study, which are used for various applications such as nonlinear optics [3–5], photovoltaics [6], biological labeling [7–10], photodynamic therapy [11] and as an exciton trap to study the excitation energy migration in luminescent organic nanoclusters [12]. Squaraines are characterized by a donor-acceptor-donor structure, showing an internal charge transfer absorption and emission band. Such a structure imparts hydrophobic properties to a squaraine molecule [1, 2, 13]. The intramolecular charge transfer characteristics combined with the extended *p*-electron donor network results in high molar extinction coefficient ($\varepsilon > 10^5$ $M^{-1}cm^{-1}$) of squaraines in the visible spectral region. Most of those dyes emit in the far visible to

the near IR spectral region and are photostable.

The dye self-association in solutions, at the solid-liquid interface or in organized media such as Langmuir-Blodgett (LB) films is an often observed phenomenon due to strong intermolecular van der Waals-like attractive forces between the molecules [14–16]. There are two limiting types of aggregates based on the orientation of transition dipoles that exhibit distinct changes in the absorption band as compared to the monomeric substances [14–16]. The first type is *J*-aggregate, with "head-to-tail" transition dipole arrangement, which is characterized by a sharp, strongly red-shifted absorption band. The second type is *H*-aggregate, characterized by a "head-to-head" transition dipole arrangement and showing a blue-shifted absorption as compared to the monomer band [14–16]. The correlation between spectral features and the aggregate structure was considered within the exciton model by Kasha [17] and Kuhn [18]. In contrast to *H*-aggregates, *J*-aggregates are fluorescent [17, 18]. It was shown that squaraines can form different kinds of aggregates (dimers, *H*-, and *J*-aggregates), depending on the structure of chromophores [14, 15].

Generally, molecular aggregation in a solution in the form of dimers or higher aggregates causes the dye fluorescence quenching due to formation of non-fluorescent *H*-dimers and *H*-aggregates [16, 19]. As a rule, addition of surfactants to a dye solution at a concentration exceeding the critical micelle concentration (CMC) prevents the dye aggregation due to the dye solubilization with surfactant micelles [19–21]. However, there are works describing the opposite effect of surfactants on a dye aggregation. It was found that the addition of cationic surfactant cetylpyridinium bromide (CPB) at concentrations exceeding the CMC causes an increasing intensity of the amphi-PIC *J*-aggregate absorption band and its narrowing [21]. Recently, a strong aggregation of cationic dye L-21 enhanced by the cationic surfactant CPB at a concentration above the CMC has been reported [22]. The aggregation enhancement of numerous cyanine dyes in solutions comprising CPB at the surfactant concentration exceeding the CMC and significant increase of *J*-aggregate luminescence quantum yield was also observed [22]. In this work, the effect of anionic surfactant sodium dodecyl sulphate (SDS) and cationic one cetylpyridinium bromide on the aggregation of a zwitterionic squaraine dye Sq–2Me (Fig. 1) in aqueous solution has been studied.

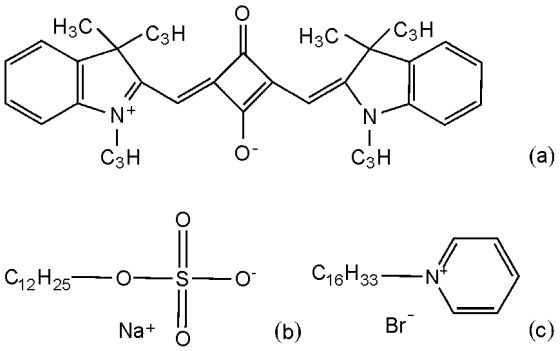

Fig. 1. Molecular structures of zwitterionic squaraine dye Sq–2Me (a), sodium dodecyl sulphate (b) and cetylpyridinium bromide (c).

Squaraine dye Sq–2Me was synthesized by Dr.I.Borovoy (Institute for Scintillation Materials, NAS of Ukraine). The dye purity was controlled by thin layer chromatography. The CPB and SDS surfactants were purchased from Sigma-Aldrich and used without additional purification. Organic solvent dimethylformamide (DMF) (Sigma-Aldrich) used to prepare the dye stock solution was of spectroscopic grade. To prepare dye dimethylformamide-water (DMF -W) binary solutions with surfactants, doubly distilled water was used. The concentrations of the surfactants in the solutions exceed their CMC values ($8 \cdot 10^{-3}$ M for SDS [24] and $6.2 \cdot 10^{-4}$ M for CPB [25]) being $1 \cdot 10^{-2}$ M and $1 \cdot 10^{-3}$ M, respectively. The concentration of Sq–2Me in all solutions was $4 \cdot 10^{-5}$ M. The Sq–2Me stock solution of $1 \cdot 10^{-3}$ M concentration was prepared in DMF. To prepare binary DMF-W dye solutions with different water content (90 or 95 %) and surfactants, the required amounts of the dye stock solution and surfactants (SDS or CPB) were mixed in a flask. Then the required amount of doubly distilled water was added.

Visible absorption spectra were registered using a USB4000 microspectrometer (Ocean Optics, USA) supplied with an incandescent lamp. The solutions were placed into a quartz cuvette of 2 mm optical length. The luminescence spectra were recorded using a spectrofluorimeter on the base of two grating monochromators MDR-23 and a xenon lamp. One of the monochromators was used to select a required wavelength (FWHM ~ 0.5 nm), the other one was used to collect the luminescence. All meas-

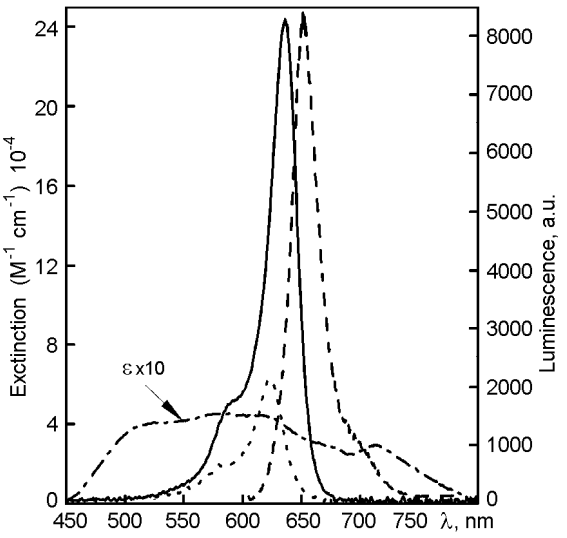

Fig. 2. Absorption spectra of Sq–2Me in DMF (solid line), DMF-W (90 %) (dotted line) and DMF-W (95 %) (dash-dotted line) binary solutions. Dashed line is the luminescence spectrum of Sq–2Me in DMF.

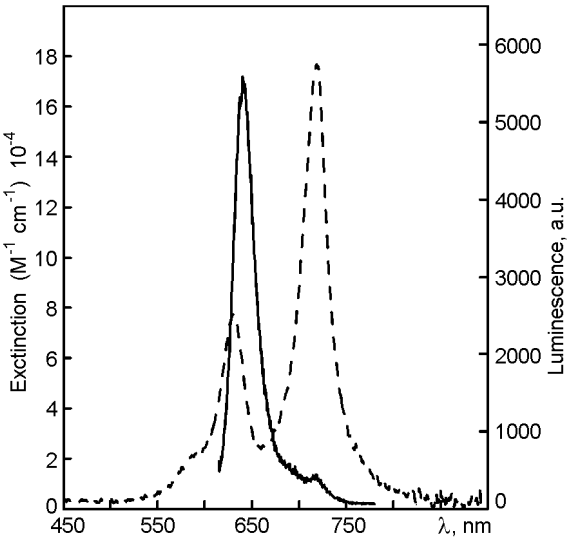

Fig. 3. Absorption (dashed line) and luminescence (solid line) spectra of Sq–2Me in a DMF-W (95 %) binary solution with SDS.

urements were done at 20°C at least in triplicate.

Absorption spectra of Sq–2Me in DMF and DMF-W binary solutions are presented in Fig. 2. The absorption spectrum in DMF exhibits a monomer peak centered at λ_{max} = 636 nm ($\varepsilon = 2.5 \cdot 10^5$ $M^{-1}cm^{-1}$) and a shoulder at 585 nm ($A_{shoulder}/A_{max} = 0.2$). In a binary DMF-W (90 %) solution, the main peak becomes weaker and blue-shifted (λ_{max} = 622 nm) that points to the solvatochromic effect [16, 19]. The ratio $A_{shoulder}/A_{max}$ in such a solution is 0.4. The luminescence intensity of Sq–2Me in a DMF-W (90 %) solution decreases significantly (not presented). The increase of water content in the binary solution up to 95 % causes a remarkable transformation of the absorption spectrum (Fig. 2). The spectrum becomes very broad, the intensities of the main peak and shoulder become equal and inseparable. The appearance of a weak peak at λ_{max} = 713 nm is also observed. The luminescence of Sq–2Me in such a solution with 95 % water content is not observed. All these facts point to the dye aggregation in the binary solution with high water content. We ascribe the main peak to the monomer band and short- and long-wavelength peaks to aggregates, the structure of those is discussed below [17, 18].

The addition of surfactants (SDS or CPB) at concentration above the CMC to a DMF-W (95 %) binary solution causes a significant transformation of the absorption spectra of Sq–2Me and a luminescence appearance (Fig. 3) that points to a strong interaction between zwitterionic dye molecules and surfactant micelles. However, solubilization of dye molecules with surfactant micelles does not prevent totally the dye aggregation. As is seen in Fig. 3, the absorption spectrum of Sq–2Me in a DMF-W (95 %) solution with SDS (dashed line) consists of three bands centered at 585, 630 and 718 nm, respectively. The luminescence spectrum consist of a band at λ_{max} = 640 nm and a shoulder at 719 nm (Fig. 3, solid line). The band at 630 nm in the absorption spectrum is the Sq–2Me monomer band red-shifted slightly in nonpolar environment as compared to that in a DMF-W (95 %) solution without surfactant (Fig. 3). The consideration of Sq–2Me absorption and luminescence spectra allows us to ascribe the short-wavelength and long-wavelength absorption bands (with respect to the monomer one) to the dye aggregates [17, 18]. It is known that the dye aggregation results in a strong coupling of the molecular transition dipoles, i.e. the electrostatic interaction between molecular transition dipoles of the chromophores causes the splitting of energy levels of the molecule excited states [17].

According to Kasha exciton theory [17], depending on the relative spatial arrangement of interacting molecules (parallel transition dipoles or in-line transition dipoles), blue-shifted *H*-band or red-shifted *J*-band

can be observed in the dye absorption spectrum. If the interacting molecules are inclined with respect to each other, two absorption bands (*H*- and *J*-band) appear in the spectrum that points to the Davydov splitting [17, 18, 26]. The ratio of their intensities depends on the angle between the molecules. The larger the angle, the more intense the *J*-band is with respect to the *H*-band [17, 18, 26]. So, the analysis of relative intensity of the aggregate absorption bands can provide information about the aggregate structure. Thus, we can ascribe the addition bands observed in the absorption spectrum (Fig. 3) to *H*- and *J*-splitting components of the dye dimer formed by two Sq–2Me molecules in SDS micelle. As the *J*-band intensity is much higher than that of *H*-band, we can conclude that the angle between the dye molecules forming the dimer is more than 90°. Our conclusion concerning the dimer origin of short-wavelength and long-wavelength absorption bands is based also on the following consideration. The concentration of micelles [*M*] in the solution can be estimated as [27]:

$$[M] = \frac{[surfactant] - CMC}{N_{agg}}, \qquad (1)$$

where [*surfactant*] is the total surfactant concentration; N_{agg}, the surfactant aggregation number (N_{agg} = 63 for SDS micelles [24] and 122 for CPB micelles [28]).

The approximate number of dye molecules (*n*) incorporated into a single micelle can be estimated [27] as

$$n = \frac{[dye]}{[M]}, \qquad (2)$$

where [*dye*] is the dye concentration in the solution.

For the solution with SDS micelles, [*M*] = $3 \cdot 10^{-5}$ M, [*dye*] = $4 \cdot 10^{-5}$ M. So, we obtain $n = 4/3 = 1.33$. In other words, one micelle contains more than one dye molecule and the formation of dye dimer in such a solution is possible. Moreover, the structure of Sq–2Me molecule is favorable to the dye aggregation [1, 2, 13]. However, the fraction of micelles containing one dye molecule is rather large. In the absorption spectrum (Fig. 3), the band corresponding to the monomer absorption is rather intense. In the luminescence spectrum of Sq–2Me in a DMF-W (95 %) solution with SDS, the monomer luminescence band (λ_{max} = 640 nm) is also intense (Fig. 3, solid line).

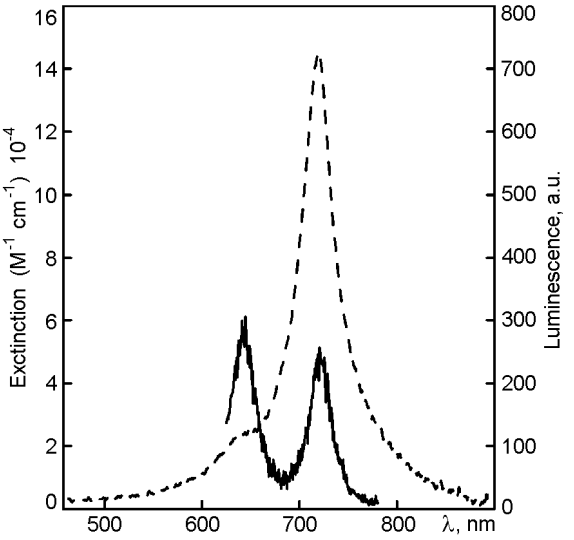

Fig. 4. Absorption (dashed line) and luminescence (solid line) spectra of Sq–2Me in a DMF-W (95 %) binary solution with CPB.

The shoulder at 719 nm (in resonance with absorption *J*-splitting component) is also observed in the luminescence spectrum; that is evidence of the fact that the dimer formed in SDS micelle possesses an inclined geometry (or a "herringbone" one) with a large angle.

It is known that the *J*-band possesses the exciton nature [29]. We can estimate the exciton delocalization length using the equation [30, 31]:

$$N_{\partial} = \frac{3}{2} \cdot \frac{\Delta\nu_m^2}{\Delta\nu_J^2} - 1, \qquad (3)$$

where $\Delta\nu_m^2$ and $\Delta\nu_J^2$ are full widths at half-maximum of monomer and *J*-aggregate absorption bands. Taking $\Delta\nu_m^2$ = 800 cm^{-1} and $\Delta\nu_J^2$ = 616 cm^{-1}, we obtain $N_{del} \sim 2$ molecules that evidences also the dimeric nature of *J*-band.

In a DMF-W (95 %) solution containing CPB micelles, the absorption and luminescence spectra of Sq–2Me differ from those in a solution with SDS micelles (Fig. 4). The absorption spectrum consists of two bands: a low-intense monomer band (λ_{max} = 633 nm) and a very intense *J*-band centered at 719 nm. That points to the fact that in this solution, the dye is mainly in associated form. Indeed, for this solution, [*M*] = $3 \cdot 10^{-6}$ M and *n* value obtained is about 13. Thus, in a DMF-W solution containing CPB micelles, a single micelle contains about 13

Sq–2Me dye molecules. That results in the formation of a more extended aggregate with J-type molecular packing (the H-band is not observed, Fig. 4, dashed line). The J-band is broader as compared to that in the solution with SDS micelles ($\Delta\nu_J$ = 854 cm^{-1} and 616 cm^{-1}, respectively). The J-band broadening in the solution with CPB micelles can be explained by the formation of J-type aggregates with different association degree. In the luminescence spectrum, the relative intensity of the monomer band is decreased considerably, that is also an evidence of the predominant dye aggregation in such a solution (Fig. 4, solid line).

To conclude, our investigations show that the addition of a surfactant of different nature (anionic or cationic) at concentrations above the CMC into a DMF-W (95 %) binary solution does not prevent the dye aggregation. In such solutions, Sq–2Me dye aggregates formation has been revealed. The structure of Sq–2Me aggregates formed in SDS and CPB micelles is different and has been discussed using the exciton theory. In a solution containing SDS micelles, the Sq–2Me dye forms dimers of "herringbone" geometry with a large angle, while in a solution with CPB micelles, the formation of more extended aggregates of J-type molecular packing with different association degree is assumed.

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Вплив поверхнево-активних речовин на молекулярну агрегацію скваранового барвника Sq–2Me у водних розчинах

С.Л.Єфімова, Г.Я.Гуральчук, А.С.Лєбєдь, О.В.Сорокін, Ю.В.Малюкін, І.Ю.Курильченко

У водних розчинах методами оптичної спектроскопії вивчено вплив аніонної (додецилсульфат натрію, SDS) та катіонної (цетилпіридиній бромід, CPB) поверхнево-активних речовин (ПАР) на агрегацію скваранового барвника Sq–2Me. Встановлено, що додавання у бінарний розчин ДМФ-В (95 %) ПАР у концентрації, вищій за критичну концентрацію міцелоутворення, не перешкоджає агрегації барвника. Структуру агрегатів барвника Sq–2Me, що утворюються у міцелах ПАР, розглянуто у рамках екситонної теорії. Отримані результати дозволяють зробити висновок, що структурою агрегатів Sq–2Me можна керувати за допомогою ПАР різної хімічної будови.