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Spectroscopic studies of dye-surfactant interactions in aqueous solutions in pre- and post-micelle formation concentration ranges

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The interaction between cationic dialkyloxacarbocyanine perchlorate ($DiOC_n$) dyes with different alkyl chain length and anionic surfactant sodium dodecylsulfate (SDS) has been studied spectrophotometrically in aqueous solutions in surfactant pre- and post-micellar concentrations (CMC). In aqueous solutions of $DiOC_2$ with SDS at SDS concentrations far before the CMC, the formation of ion-pair complexes of 1:1 composition between dye cations and surfactant anions has been revealed. Using absorption spectra of the dyes in solutions at SDS concentration above the CMC, binding constants (K_b) of the dyes to the surfactant micelles and fraction of the dyes bound to the micelles (f_{mic}) have been calculated by means of the Benesi-Hildebrand equation. It has been shown that binding of oppositely charged dyes and surfactant micelles is controlled by both electrostatic and hydrophobic forces. However, even a small increase in the dye alkyl chain length causes an abrupt nonlinear increase of the f_{mic} value that points to the fact that the hydrophobic interactions plays a major role in the dye to micelle incorporation.

Методами спектроскопии в водных растворах исследованы взаимодействия между катионными красителями диалкилоксакарбоцианин-перхлоратами ($ДиОК_n$) с различной длинной углеводородных радикалов и анионным поверхностно-активным веществом (ПАВ) додецилсульфатом натрия (НДС), при концентрации последнего ниже и выше критической концентрации мицеллообразования (ККМ). В водных растворах $ДиОК_n$ с НДС при концентрации НДС намного ниже ККМ наблюдалось образование комплексов состава 1:1 между катионом красителя и анионом ПАВ. Из спектров поглощения красителей в водных растворах при концентрации ПАВ выше КМК, с использованием уравнения Бенеши-Гильдебранда определены константы связывания красителей с мицеллами НДС (K_b) и доли связанных красителей (f_{mic}). Показано, что связывание противоположно заряженных красителя и мицелл ПАВ определяется как электростатическими, так и гидрофобными взаимодействиями. Однако тот факт, что даже небольшое увеличение гидрофобности красителя за счет увеличения длины углеводородного радикала приводит к резкому нелинейному увеличению значения f_{mic}, свидетельствует о том, что ключевую роль играют гидрофобные взаимодействия.

Dye-surfactant interaction is considered in numerous studies [1–14]. The surfactant micelles containing polar and hydrophobic fragments and being formed in solutions at the surfactant concentration exceeding the critical micelle concentration (CMC), are considered to be simple model systems of biological membranes, because cell membranes consist of surface-active components (lipid bilayers) [15]. The micelles and other colloidal and macromolecular systems have been extensively employed as model systems to investigate the effects of heterogeneous environments and microenvironments on a

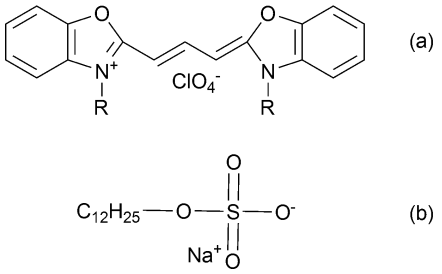

Fig. 1. (a) Chemical structure of the $DiOC_n$ dyes. R = C_2H_5: 3,3′-diethyloxacarbocyanine perchlorate ($DiOC_2$), R = C_6H_{13}: 3,3′-dihexyloxacarbocyanine perchlorate ($DiOC_6$); R = C_9H_{19}: 3,3′-dinonyloxacarbocyanine perchlorate; R = $C_{18}H_{37}$: 3,3′-dioctadecyloxacarbocyanine perchlorate ($DiOC_{18}$); (b) Structural formula of surfactant sodium dodecylsulfate (SDS).

wide variety of reactions [16–20]. The study of interactions between organic molecules and surfactant micelles can help to understand the complex processes of substance delivery and transport taking place in various biological processes. Optical analysis based on fluorescent labeling has been extensively used to study these processes and organic fluorophors are used most often for these purposes [21, 22]. Therefore, studying the interaction between dyes and surfactant micelles is also important from this standpoint. For instance, it was noted that the hydrophobicity of fluorophors influences the efficiency of living cell staining and tracing [23]. It was found that less hydrophobic fluorophors bind less effectively to the cell organelles and can diffuse into a cell cytoplasm during cell tracing [23].

In this work, the interaction between a series of cationic carbocyanine dyes ($DiOC_n$) with different alkyl chain length (Fig. 1) and anionic surfactant sodium dodecylsulphate (SDS) has been studied in aqueous solutions in pre- and post-micellar concentrations by means of spectroscopic measurements. The method of continuous variations was used to study the ion-pair complex formation in pre-micellar range [10, 24]. The binding constants and the fraction of dye bound to SDS micelles in post-micellar range were calculated using the Benesi-Hildebrand equation [25–27] which can be applied at high surfactant concentrations [11, 12]. The effect of dye alkyl chain length on binding constants of the cationic dye to anionic SDS micelles has been studied. Carbocyanine dyes 3,3′-diethyloxacarbocyanine perchlorate ($DiOC_2$), 3,3′-dihexyloxacarbocyanine perchlorate ($DiOC_6$), 3,3′-dinonyloxacarbocyanine perchlorate ($DiOC_9$), and 3,3′-dioctadecyloxacarbocyanine perchlorate ($DiOC_{18}$) were synthesized by Dr.I.Borovoy (Institute for Scintillation Materials, NAS of Ukraine). The purity of the dyes was controlled by thin layer chromatography. The surfactant SDS was purchased from Sigma Aldrich and used without purification. Ethanol used to prepare stock solutions of dyes and surfactants was a spectroscopic grade product. To prepare aqueous solution of the dyes with surfactants for the investigations, doubly distilled water was used. The surfactant concentration was varied in the concentration range of $1 \cdot 10^{-6}$ M to $5 \cdot 10^{-2}$ M.

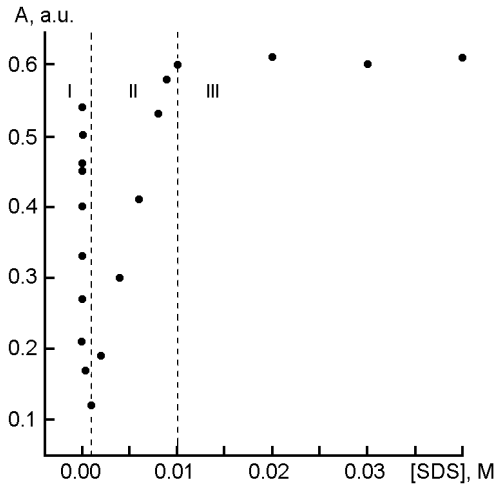

Fig. 2. Effect of SDS on the absorbance of $DiOC_2$ dye. The dye concentration in all solutions is $2 \cdot 10^{-5}$ M.

The stock solutions of each dye of $1 \cdot 10^{-3}$ M concentration were prepared in ethanol. Since the SDS concentration is varied in a wide range, to prepare aqueous solutions with small amount of SDS, a stock SDS solution in ethanol of $1 \cdot 10^{-3}$ M was needed. To prepare aqueous solutions of the dyes with surfactant, the required amounts of stock dye and SDS solutions in ethanol at a certain ratio were placed in a flask and ethanol was evaporated. Then the required amount of doubly distilled water was added.

Visible absorption spectra were recorded using a UV-Visible Spectrophotometer (Specord 200, Analytik, Jena) and a quartz cell of 2 mm optical length. All measurements were done at 20°C at least in triplicate.

The cationic dyes $DiOC_n$ possess the same chromophore fragment and differ in the

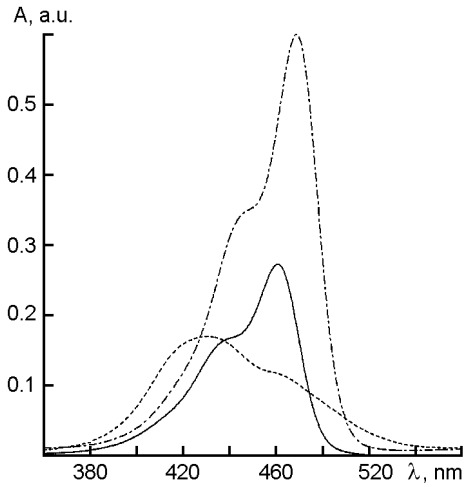

Fig. 3. Absorption spectra of $DiOC_2$ dye in aqueous solutions at different surfactant concentrations: without SDS (solid line); $1 \cdot 10^{-3}$ M (dashed line); $1 \cdot 10^{-2}$ M (dash-and-dotted line). The dye concentration in all solutions is $2 \cdot 10^{-5}$ M.

length of alkyl chains only (Fig. 1). The alkyl chain length governs the dye hydrophobicity which increases with increasing chain length.

At the work first stage, the interaction of less hydrophobic dye $DiOC_2$ with SDS was studied in pre- and post-micellar regions. For this purpose, the absorption spectra of $DiOC_2$ were studied in aqueous solution with SDS at concentrations varied from $1 \cdot 10^{-6}$ M to $5 \cdot 10^{-2}$ M (Fig. 2). $DiOC_2$ is a water-soluble organic dye. In aqueous solutions, the Lambert-Beer law is valid in the dye concentration range $1 \cdot 10^{-5}$–$1 \cdot 10^{-4}$ M. In these experiments, the dye concentration was $2 \cdot 10^{-5}$ M. The changes in the dye absorption were detected at $\lambda_{max} = 480$ nm.

Fig. 2 shows that the curve of absorption changes depending on the SDS concentration could be divided into three regions. Within region I, which corresponds to the SDS concentration from $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-3}$ M, the 480 nm absorption band intensity decreases gradually. At the same time, the appearance of a new short-wavelength band at 450 nm is observed (Fig. 3). The decrease in the absorbance at 488 nm and the appearance of the new band at the surfactant concentration below the CMC (for SDS, CMC = $8 \cdot 10^{-3}$ M [28]) indicate the molecular complex formation between cationic dye $DiOC_2$ and anionic surfactant molecules due to electrostatic interaction [1, 10–13].

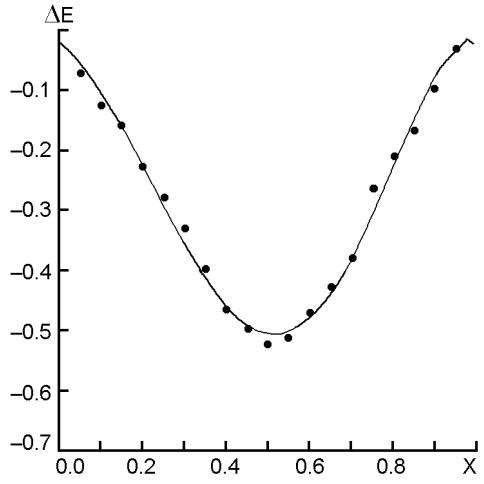

Fig. 4. The Job's plot of $DiOC_2$ and SDS at 20°C.

The reaction between the dye (D) and the surfactant (S) can be described as an equilibrium reaction:

$$xD + yS \rightleftarrows D_xS_y.$$

The method of continuous variation, or the Job's method, is one of the most common techniques used in complex ion studies [10, 24]. This method allows the stoichiometric composition of the complex to be determined. For this purpose, the mother aqueous solutions of the dye C_D^0 and the surfactant C_S^0 should be prepared in equal concentrations. In our study, $C_D^0 = C_S^0 = 1 \cdot 10^{-4}$ M. The mother solutions are mixed in varying volume ratios, but in such a way that the total volume of each mixture remains the same x volume units of the dye solution added to $(1-x)$ volume units of the surfactant solution ($x<1$) [10, 24]. A series of mixed solutions is prepared and the absorbance (E) of the each solution is measured. A Job's plot is obtained by plotting the corrected absorbance of each mixture ΔE versus the dye volume fraction (x). The corrected absorbance can be calculated using the following equation [10]:

$$\Delta E = E_{\text{exp}} - \varepsilon_D c_D^0 l x, \qquad (1)$$

where $\varepsilon_D c_D^0 l$ is the absorbance of the dye solution without surfactant ($x = 1$).

The volume ratio x that corresponds to the minimum in the Job's plot is the combining ratio of surfactant and the dye in the associate [10, 24].

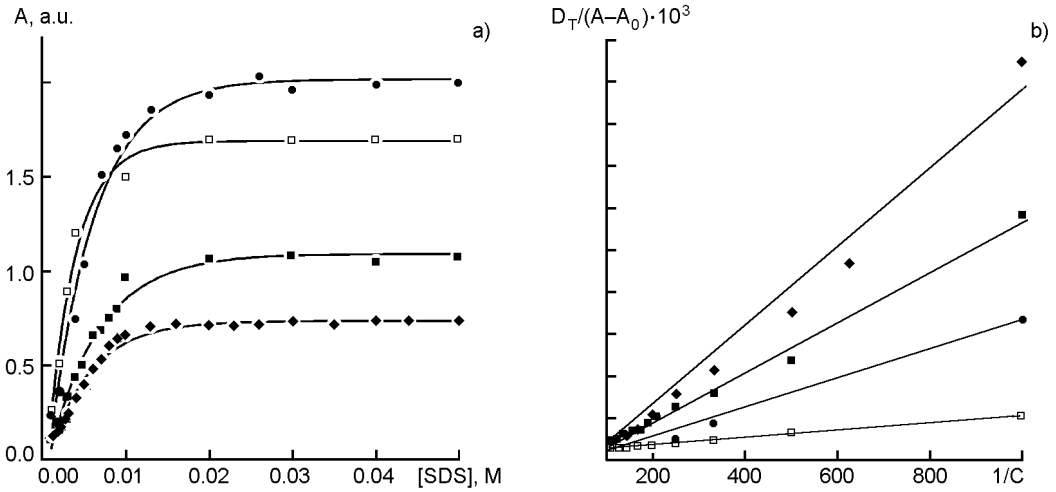

Fig. 5. (a) The change of $DiOC_2$ (■), $DiOC_6$ (●), $DiOC_9$ (◆) and $DiOC_{18}$ (□) absorbance as a function of SDS concentration; (b) The Benesi-Hildebrand plots for $DiOC_2$ (■), $DiOC_6$ (●), $DiOC_9$ (◆) and $DiOC_{18}$ (□) binding to SDS micelles.

The Job's plot of $DiOC_2$ and SDS at 20°C is presented in Fig. 4. The minimum at $x = 0.5$ means that 1:1 associates are formed. So, we can conclude that the short-wavelength absorption band formed in the solution at the surfactant concentration far before the CMC (region I) corresponds the dye-surfactant complex formation with 1:1 stoichiometry.

At the SDS concentrations $1\cdot10^{-3}$–$1\cdot10^{-2}$ M (Fig. 2, region II), a sharp increase of the $DiOC_2$ absorption and a red shift of the absorption maximum to 488 nm with increasing SDS concentration were observed that points to the onset of the micelle formation and the dye incorporation to SDS micelles (Figs. 2, 3) [11, 29–32]. In region III corresponding to the SDS concentrations from $1\cdot10^{-2}$ M to $5\cdot10^{-2}$ M, the absorbance of $DiOC_2$ does not change, thus pointing that all dye molecules are incorporated to surfactant micelles (Fig. 2). The SDS concentration of $1\cdot10^{-3}$ M at which the sharp increase in the dye absorption and the red shift of the absorption maxima are observed is considered as the CMC of SDS in an aqueous solution in the presence of the dye [11, 32]. The lower value of the CMC than that obtained by other methods in pure aqueous solutions ($8\cdot10^{-3}$ M [28]) is the result of dye-surfactant interactions. The process of micelle formation is known to be sensitive to small changes in ionic strength of the aqueous solution [1, 28]. Additives, such as alcohols, salts, organic molecules, etc., can change the surfactant CMC value in solutions. In general, organic molecules (or ions) tend to reduce the CMC [1, 28]. The CMC value obtained for SDS in the aqueous solution in the presence of the dye is in agreement with this statement.

At the second stage, the efficiency of the dye-surfactant micelle interaction was studied depending on the dye hydrophobicity.

The dye-micelle interaction can be described as an equilibrium reaction:

$$D + M \overset{K_b}{\rightleftarrows} DM$$

where D, M and DM are the dye, micelle and dye-micelle associate, respectively; K_b, the binding constant. To determine K_b, the Benesi-Hildebrand equation in the following modified form was used [10–12]:

$$\frac{D_T}{A_0 - A} = \frac{1}{\varepsilon_m - \varepsilon_0} + \frac{1}{K_b(\varepsilon_m - \varepsilon_0)C_m}, \qquad (2)$$

where D_T is the total dye concentration in the solutions ($2\cdot10^{-5}$ M); A and A_0, the dye absorbance in the presence and absence of SDS, respectively; ε_0, the dye molar extinction coefficient in aqueous solutions without the surfactant; ε_m, that of the dye fully bound to the micelles; C_m is the concentration of the micellized surfactant ([surfactant]-CMC). The plot of $D_T/(A_0-A)$ against $1/C_m$ is linear, K_b and ε_m can be obtained from the line slope and intercept, respectively.

Since $DiOC_6$, $DiOC_9$ and $DiOC_{18}$ dyes possess hydrophobic properties, in pure aqueous solutions they form aggregates; the SDS concentration of $1 \cdot 10^{-3}$ M was considered as the CMC for the solutions with all dyes. To calculate the binding constants of the dyes to SDS micelles, regions II and III of the surfactant concentrations were analyzed for all dyes (Fig. 2).

For each dye, the 480 nm absorbance changes depending on the SDS concentration were analyzed (Fig. 5a). For each dye, the SDS concentration increasing from $1 \cdot 10^{-3}$ M to $5 \cdot 10^{-2}$ M causes an increase in the dye absorbance and a red shift (to 488 nm) of the absorption maximum (Fig. 5a). The red shift of the absorption maxima in a less polar medium is a direct indication of the dye incorporation to SDS micelles [1, 11, 29–32]. The plot of $D_T/(A_0-A)$ against $1/C_m$ was revealed to be linear for all dyes (Fig. 5b). The K_b and ε_m values obtained using least square analysis are given in Table. The K_b value increases with increasing alkyl chain length of the dye. In other words, the alkyl chain length of the dye molecule influences substantially the dye binding to a surfactant micelle. The Coulomb interactions between a positively charged dye molecule and a negatively charged SDS micelle do not play a major role in the dye-micelle binding. Apparently, their major function is to bring the dye cation and the surfactant micelle close enough at the process onset to enable the action of hydrophobic interactions which are finally responsible for the dye-micelle binding [5]. As it seen from Table, the dye with the longer alkyl chain (more hydrophobic) reveals a stronger trend to bind to a surfactant micelle.

To estimate the efficiency of the dye-micelle binding, the fraction of micellized dye molecules (f_{mic}) was calculated [7, 12]:

$$f_{mic} = \frac{K_b[M]}{1 + K_b[M]}, \qquad (3)$$

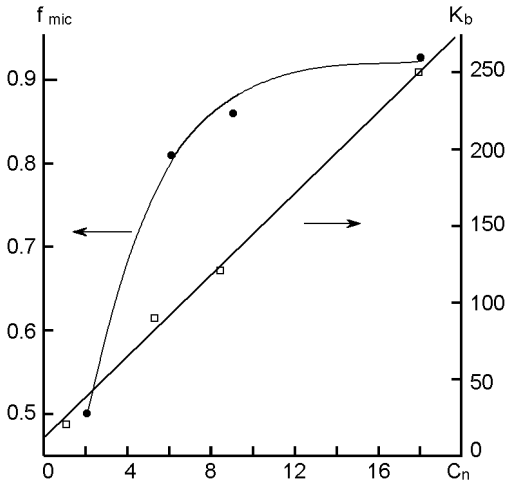

Fig. 6. Dependences of f_{mic} (•) and K_b (□) on the number of carbon atoms in dye alkyl chains (C_n).

where K_b is the binding constant; $[M]$, the surfactant concentration at which the maximum number of dye molecules bind to the micelles ($5 \cdot 10^{-2}$ M). The obtained values are listed in Table.

The dependences of obtained K_b and f_{mic} values on the dye alkyl chain length is presented in Fig. 6 which indicates the linear dependence of K_b on the number of hydrocarbon atoms in alkyl chains of the dyes. At the same time, the fraction of micellized dye molecules (f_{mic}) changes not linearly. In a case of $DiOC_2$ (less hydrophobic dye), only 50 % of the dye are bound to the SDS micelle. A small increase in the dye hydrophobicity results in a sharp increase of the amount of bound dye (81 % for $DiOC_6$) and then the curve f_{mic} vs C_n reaches saturation (Fig. 6). This indicates that in spite of Coulumb interaction between the oppositely charged dye and SDS micelle, the hydrophobic interactions play the major role in the cationic dye-anionic micelle interaction.

To conclude, using absorption spectroscopy, cationic dye-anionic surfactant inter-

Table. Spectroscopic properties of $DiOC_n$ dyes in aqueous solutions with SDS at 293 K

Dye	ε_0^a, $M^{-1} \cdot cm^{-1}$	ε_m, $M^{-1} \cdot cm^{-1}$	K_b (M^{-1})	f_{mic}
$DiOC_2$	10500	52500	20	0.50
$DiOC_6$	15000	31000	90	0.81
$DiOC_9$	8125	12000	120	0.86
$DiOC_{18}$	17000	41000	250	0.93

[a] ε_0 values were calculated at surfactant concentration of $1 \cdot 10^{-3}$ M (CMC, "zero" point).

actions have been studied in aqueous solutions in surfactant pre- and post-micellar concentration ranges. The addition of anionic surfactant SDS into the $DiOC_2$ aqueous solution causes an essential changes in the dye absorption spectra. At SDS concentrations far lower than the CMC, the formation of ion-pair complexes of 1:1 composition between dye cations and surfactant anions has been revealed. The SDS concentration increase above the CMC results in increased absorption intensity for all dyes and shift of the absorption maxima toward longer wavelengths that are evidences of the dye incorporation into SDS micelles. It has been found that the interaction of oppositely charged dyes and surfactant micelles is controlled by both electrostatic and hydrophobic interactions. The increase of the dye hydrophobicity due to lengthening alkyl chain increases the trend to association, the K_b, f_{mic} values increase with increasing dye alkyl chain length. For $DiOC_2$ dye with the shortest alkyl chains, the electrostatic attraction between the dye and a micelle is found to be not sufficient for effective binding. In this case, only 50 % of the dye molecules are incorporated into SDS micelles. However, a small increase in the dye alkyl chain length causes an abrupt nonlinear increase of the f_{mic} value that points to the fact that the hydrophobic interactions play a major role in the dye-to-micelle incorporation.

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Спектроскопія взаємодій між барвником та поверхнево-активною речовиною у водних розчинах до та після міцелоутворення

С.Єфімова

Методами оптичної спектроскопії у водних розчинах досліджено взаємодію між катіонними барвниками діалкілоксакарбоціанін-перхлоратами (ДіОК$_n$) з різною довжиною вуглеводневих радикалів та аніонною поверхнево-активною речовиною (ПАР) додецилсульфатом натрію (НДС) в концентрації останнього нижче та вище критичної концентрації міцелоутворення (ККМ). У водних розчинах ДіОК$_n$ з НДС при концентрації НДС нижче ККМ зареєстровано утворення комплексів складу 1:1 між катіоном барвника та аніоном ПАР. Зі спектрів поглинання барвників у водних розчинах при концентрації ПАР вищій від ККМ з використанням рівняння Бенеші-Гільдебранда отримано константи зв'язування барвників з міцелами НДС (K_b) та фракції зв'язаних барвників (f_{mic}). Показано, що зв'язування протилежно заряджених барвника та ПАР зумовлено як електростатичними, так і гідрофобними взаємодіями. Однак той факт, що навіть невелике збільшення гідрофобності барвника за рахунок збільшення довжини вуглеводневого радикалу призводить до різкого нелінійного зростання величини f_{mic}, свідчить про те, що гідрофобні взаємодії відіграють ключову роль.