

Solubilization of Cationic Hemicyanine Dyes in Anionic Surfactant Micelles: A Partitioning Study

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Summary. Cationic hemicyanine dyes of the 1-methyl-4-(4-(di-*n*-alkylamino)-styryl) pyridinium betain type (alkyl group = methyl to butyl) have been investigated by differential spectroscopy in order to ascertain their solubilization in aqueous micellar solution of sodium dodecylbenzene sulfonate (*SDBS*). The differential absorption spectra were recorded as a function of surfactant concentration at 25.0°C. Thermodynamic parameters were calculated from partition coefficient data. The results show that cationic hemicyanine dyes are solubilized at the micellar surface, indicating an electrostatic interaction between dyes and surfactant micelles.

Keywords. Absorption spectra; Dyes; Partition coefficient; *SDBS*; Solubilization.

Introduction

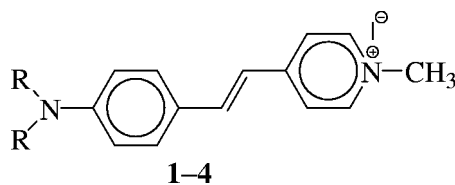
Organized assemblies of surfactants in aqueous solution *i.e.* micelles, have a remarkable effect on the solubility of some organic substances, which are otherwise sparingly soluble in water. The phenomenon of solubilization [1] plays an important role in detergency [2] and in pharmaceutical applications [3]. Solubilization has been treated as partitioning of additive molecules between a micellar phase and an intermolecular bulk phase [4–6]. The partitioning behaviour of additives between the aqueous and the micellar phase is an indication of the hydrophilic-lipophilic balance of the molecules. The interactions between additive and water, additive and micelles, and water and micellar phase play a vital role in the partitioning process.

The thermodynamic process of the transfer of the additive between different media is characterized by free energy changes and partition coefficients, respectively. The partition coefficient depends on the structure of the additive and the surfactant that constitutes the micelles. Among the various factors that undoubtedly contribute to the solubilization in micellar systems, hydrophobic contributions are quite significant [4, 7]. Hemicyanine dyes, among other heterocyclic dyes, have been employed to study biological systems [8] and, being effective voltage sensitive probes in biomembranes, are frequently used to follow the fast changes of electrical

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potential in neurons [9]. However, the use of cationic hemicyanine dyes is less common than that of their zwitterionic analogues.

Previously, we have reported the solubilization of short chain phenylalkanoic acids [10], zwitterionic hemicyanine dyes [11–13], and cationic hemicyanine dyes [14] in aqueous micellized solutions of anionic and cationic surfactant systems. In the present investigation we have examined the solubilization of cationic hemicyanine dyes of the betain type (1-methyl-4-(4-(di-*n*-alkylamino)-styryl)pyridinium betains), dissolved in aqueous solutions of sodium dodecylbenzene sulfonate (*SDBS*). The general structure of the dyes used is given below ($R = \text{CH}_3$ to C_4H_9 for **1–4**)



The water-micelle partition coefficient (K_x), the standard free energy change of solubilization, (ΔG_p°), and other related parameters were determined by differential absorption spectroscopy [15] at 25.0°C.

Results and Discussion

The differential absorption spectra intensity of solutions of **3** increases with increasing surfactant concentration of *SDBS* (Fig. 1). The differential absorbance

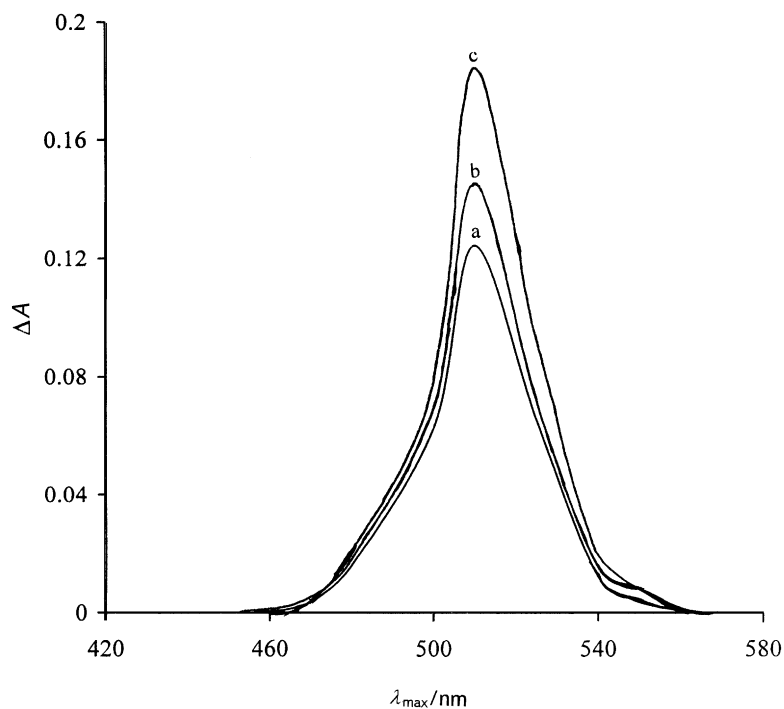
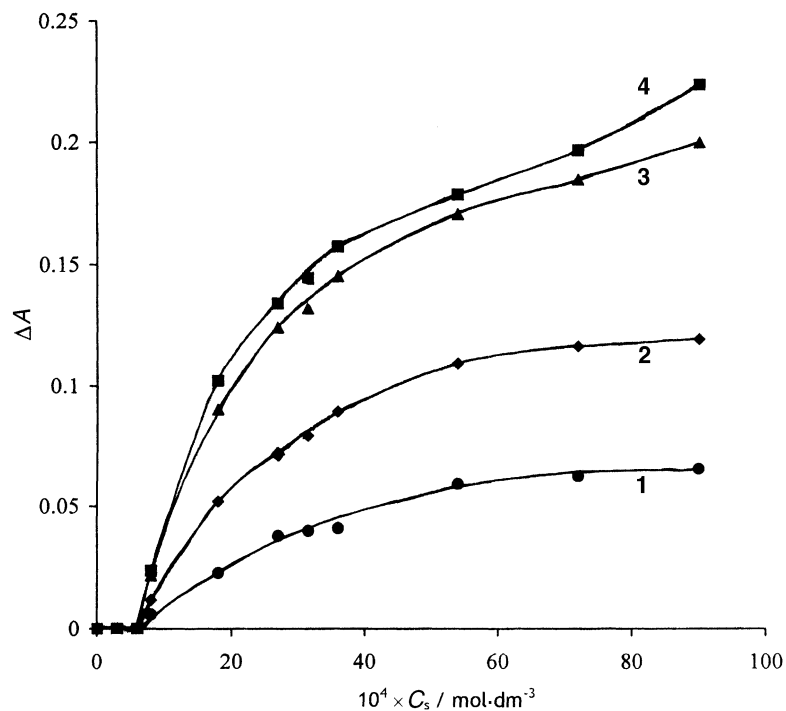


Fig. 1. Differential absorption spectra of $1.0 \times 10^{-5} \text{ mol/dm}^3$ solution of **3** in *SDBS*; [*SDBS*] = $C_s \times 10^4 \text{ mol/dm}^3$: $a = 27.0$, $b = 36.0$, $c = 72.0$

Table 1. λ_{\max} , K_c , K_x , and $-\Delta G_p^\circ$ for cationic hemicyanine dyes in *SDBS* micelles

Dye	λ_{\max}/nm	$K_c/\text{dm}^3 \cdot \text{mol}^{-1}$	K_x	$-\Delta G_p^\circ/\text{kJ} \cdot \text{mol}^{-1}$
1	508.2	318.67	17686	24.23
2	498.3	385.56	21399	24.70
3	509.8	473.77	26294	25.21
4	501.3	478.92	26580	25.24

**Fig. 2.** Differential absorbance (ΔA) for cationic hemicyanine dyes at various concentrations of *SDBS*

was recorded at the wavelength of the highest peak in the spectra. The shift of each peak with increasing surfactant concentration can be ignored within experimental error (± 0.6 nm). λ_{\max} , for the respective dyes is shown in Table 1. The increase in absorbance with increasing surfactant concentration is regarded to be caused by penetration of the dye molecules into the micelles as observed in other cases [4, 10–16].

The dependence of ΔA (differential absorbance) of the cationic hemicyanine dyes solutions with the increasing C_s (surfactant concentration) illustrates that ΔA is zero in the pre-micellar region of the surfactant (Fig. 2). As the *SDBS* concentration increases, ΔA increases above a certain value of C_s which is regarded as the critical micelle concentration (*CMC*). Both Figs. 1 and 2 directly indicate the solubilization of dye in micelles. Although the dye molecules are incorporated in the micelles, their chromophores are still oriented near the surface and hence absorb light more

favorably than in the aqueous bulk solution [16]. More hydrophobic dyes displayed a higher increase in ΔA than less hydrophobic dyes.

It is suggested that the additives are partitioned between surfactant micelles and the bulk water phase obeying the partition law [17]. The partition coefficients of the cationic hemicyanine dyes were determined by the differential absorbance method as reported by *Kawamura et al.* [15], suggesting that *Lambert-Beer's* law holds for the solubilized additive. The relationship used to determine the water-micelle partition coefficient is given in Eq. (1), where ΔA_∞ is the differential absorbance obtained from the intercept of Fig. 3 by extrapolating to very high concentrations (C_s) of the surfactants, C_a is the dye concentration, and C_s^{mo} represents the analytical concentration of micellized surfactant, *i.e.* $C_s - CMC_o$ (CMC_o is the *CMC* of *SDBS* in pure water).

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_a + C_s^{mo})} + \frac{1}{\Delta A_\infty} \quad (1)$$

The units of K_c in Eq. (1) are dm^3/mol . K_c is related to K_x via $K_x = K_c n_w$ (n_w is the amount of water per dm^3 , *i.e.* $55.5 \text{ mol}/\text{dm}^3$). The plot of $1/\Delta A$ vs. $1/(C_a + C_s^{mo})$ for cationic hemicyanine dyes at a certain concentration of the dye ($C_a = 1.0 \times 10^{-5} \text{ mol}/\text{dm}^3$) gives the values of ΔA_∞ and K_c (Fig. 3). The value of K_x increases with the length of the alkyl chains of the dyes. This indicates an increase in equilibrium distribution of the dye molecules which are transferred into the micellar phase more favorably with increasing hydrophobicity as also observed in other cases [18].

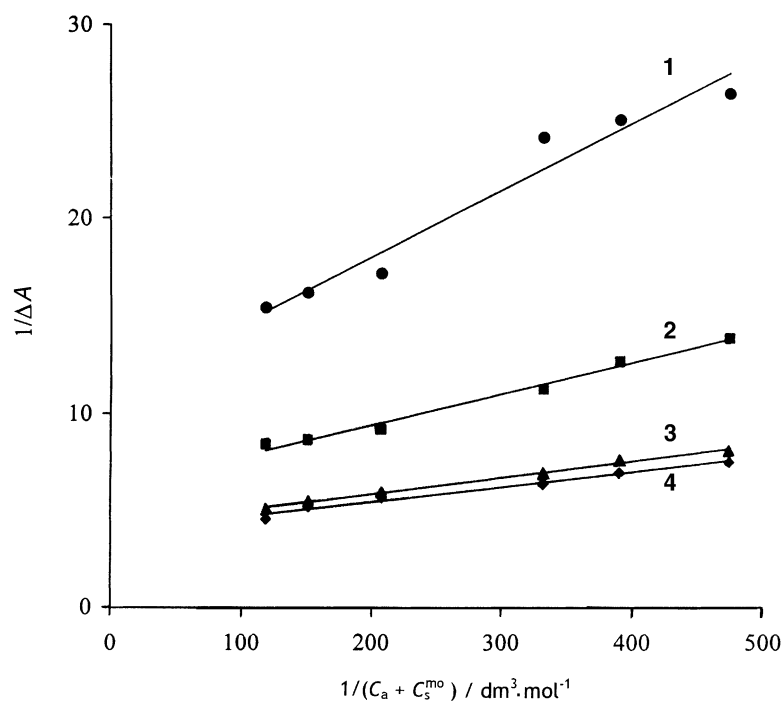


Fig. 3. Relationship between $1/\Delta A$ and $1/(C_a + C_s^{mo})$ for cationic hemicyanine dyes

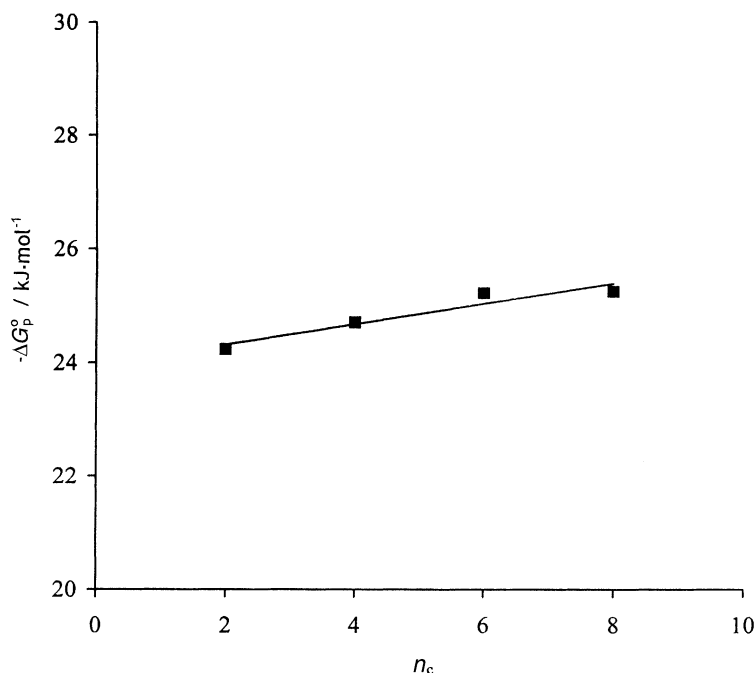


Fig. 4. Dependence of $-\Delta G_p^\circ$ of cationic hemicyanine dyes on the number of methylene group (n_c)

The standard free energy change, ΔG_p° , of the transfer of the dyes from the bulk water phase to the micellar phase is given by the well-known relationship

$$\Delta G_p^\circ = -RT \ln K_x \quad (2)$$

The values of ΔG_p° for all dyes together with K_x are summarized in Table 1. The ΔG_p° values become more negative as we go from dye **1** to dye **4**, indicating enhanced solubility of more hydrophobic dyes inside the micelles. The Gibbs free energy change of transfer per methylene group, $\Delta G^\circ(\text{CH}_2)$, from the bulk water phase to the micellar phase was evaluated from the slope of the line obtained by a plot of ΔG_p° vs. the number of carbon atoms (n_c) in the hydrocarbon chain of the dye (Fig. 4).

$\Delta G^\circ(\text{CH}_2)$ values for the migration from water to ionic micelles have been reported as $-1296 \text{ J}\cdot\text{mol}^{-1}$ for alkyl phenoxide ions and alkyl phenol and $-1254 \text{ J}\cdot\text{mol}^{-1}$ for benzoic acid and aniline [4]. $\Delta G^\circ(\text{CH}_2)$ of the same compounds from water to *n*-heptane is near $-3762 \text{ J}\cdot\text{mol}^{-1}$ [7]. These results suggest that the compounds were solubilized within the polar environment, such as the water-micelle interface [7]. $\Delta G^\circ(\text{CH}_2)$ for cationic dyes in a *SDBS* micellar solution was found to be $-180 \text{ J}\cdot\text{mol}^{-1}$. The negative value of $\Delta G^\circ(\text{CH}_2)$ indicates that the solubilization of cationic hemicyanine dyes into micelles is thermodynamically favoured. The $\Delta G^\circ(\text{CH}_2)$ value suggests that the methylene group (CH_2) in a molecule of cationic dye contributes $-180 \text{ J}\cdot\text{mol}^{-1}$ of energy during the process of solubilization in *SDBS* micelles. In the view of the above results it may be concluded that the cationic hemicyanine dyes are solubilized within polar environments that prevail near the water-micelle interface region.

Table 2. *j* values for cationic hemicyanine dyes at various concentrations of *SDBS*

$10^4 \times C_s / \text{mol} \cdot \text{dm}^{-3}$	<i>j</i>			
	1	2	3	4
8.00	0.066	0.074	0.090	0.091
18.0	0.254	0.321	0.367	0.386
27.0	0.419	0.444	0.505	0.507
31.5	0.441	0.487	0.538	0.545
36.0	0.452	0.549	0.591	0.594
54.0	0.650	0.672	0.693	0.673
72.0	0.684	0.716	0.750	0.742
90.0	0.717	0.734	0.811	0.844

The fraction of the amount of solubilized dye in the micelles to that of added dye, *j*, can be evaluated from Eq. (3) [15].

$$j = \frac{\Delta A}{\Delta A_{\infty}} \quad (3)$$

The *j* values were calculated using ΔA_{∞} obtained from the intercept of the plot of Eq. (1) and are given in Table 2. The value of *j* increases with increasing surfactant concentration and increasing hydrophobicity of the dyes.

The K_x values are intrinsically valuable, being indicative for the interaction of the additive with the micelles and the site of solubilization. The extent of solubilization depends on the structure of the additive molecule that may penetrate deeply into the hydrocarbon core or remain adsorbed at the polar surface of the micelle. Polar additives tend to solubilize with a strong interaction between polar group and ionic head group of surfactants. In this study, the K_x values are consistent with other physical evidence and indicate that the head group of these polar dye molecules are anchored in the surface region of the surfactant micelles, whereas their aliphatic and aromatic moieties extend partially into the hydrophobic core of the micelles. The partitioning of the dye molecules between the bulk water and the micellar phase depends on their hydrophobicity as well as their polarity. Ionic surfactants can interact electrostatically with polar additives because the large surface charge densities of the micelles lead to strong ion-dipole interactions [19]. In addition, ionic micelles ordinarily have an extensive hydrophobic core region that can interact with alkyl chains of additives. Hydrophobic effects have often been treated extensively [4, 7], but the effect of electrostatic interaction should also be considered in relation to the solubilization of organic additives in ionic micelles.

The values of K_x and $-\Delta G_p^{\circ}$ of the dyes increase with increasing dye hydrophobicity. The magnitude of K_x , $-\Delta G_p^{\circ}$, and $\Delta G^{\circ}(\text{CH}_2)$ reveals that the interaction at the head group is favored with increasing hydrophobicity of the dyes. The dye molecules find a more favorable orientation for interaction near the surfactant head group when they contain a longer dialkyl chain attached to the amino grouping (**3**, **4**). It has been suggested that dye molecules interact with the head group of the surfactant micelles, and complex formation takes place [20]. At first adhesion of the dye-surfactant complex to the micelle surface occurs, followed by

reorientation of the dye into the inner micellar core through hydrophobic interactions as observed with the anthraquinoid dye [16]. More hydrophobic dyes exhibit stronger interaction with the micelle and make their way deep into the interior of the micelle more actively. *SDBS*, which contains a negative charge, interacts with the positive charge present on the dye molecule and, in turn, the dye molecule is trapped easily into the micelle where its hydrocarbon chain interacts with the hydrophobic core of the micelles. Earlier, we have shown that the solubilization of these cationic hemicyanine dyes in ionic micelles is due to the electrostatic interactions between dyes and surfactant micelles rather than to the hydrophobicity of the dyes [14].

Experimental

The *trans*-cationic hemicyanine dyes used in this work have been prepared previously [14]. *SDBS* was obtained from Fluka and used without further purification. The water used was distilled twice from alkaline permanganate.

Solutions of cationic hemicyanine dyes of a particular concentration ($C_a = 1.0 \times 10^{-5} \text{ mol/dm}^3$) were prepared. The surfactant solutions were prepared by using dye solution as solvent. The differential absorption spectra were recorded with a Hitachi model 220 UV/Vis spectrophotometer. All spectra were recorded at $25.0^\circ\text{C} (\pm 0.1^\circ\text{C})$ using dye solution as reference. The concentration of dye was kept constant throughout the experiment.

The critical micelle concentration (*CMC*) of *SDBS* was obtained from a plot of specific conductivity vs. surfactant concentration without dye. The specific conductance of the surfactant solutions was measured with a Microprocessor conductivity meter (WTW) LF 2000/C at 25.0°C . A water thermostat was used to control the temperature within $\pm 0.01^\circ\text{C}$.

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