Partition Coefficient of Amphiphilic Hemicyanine Dyes between Water and Micelles of Sodium Dodecyl Benzene Sulfonate

S.S. SHAH AND M. ALI AWAN
Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

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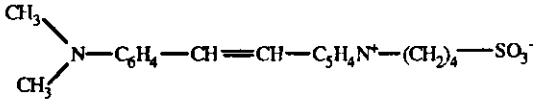
Summary: The solubilization of amphiphilic hemicyanine dyes i.e., [1] (Dimethylamino) stilbazolium butyl sulfonate, [2] (Dihexylamino) stilbazolium butyl sulfonate, into micelles of an anionic surfac ant, sodium dodecyl benzene sulfonate (SDBS), was studied as a function of SDBS concentration above the critical micelle concentration. The micelle-water partition coefficient, K_x, and the standard free energy change of solubilization, ΔG_p°, of the dyes in SDBS micelles were determined at 25.0°C by a differential spectroscopic method. The solubilization of more hydrophobic dye in micelles was greater than the less hydrophobic dye.

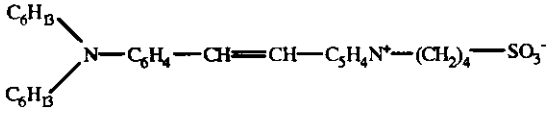
Introduction

The amphiphilic hemicyanine dyes are basically aminostilbazolium dyes. These dyes are zwitterionic in nature and are derivatives of aminostyrylphridiniura and its homologs [1]. These dyes are effective voltage sensitive probes in biomembranes and are popular fluorescence indicators of fast voltages transients in neurons, in culture and in brain [2]. The probing of fast changes of the electrical potential in biological membranes is studied extensively in the light of photophysical properties of the dyes [1,2]. The structures of the dyes used in present work are given below:

Dye I: (Dimethylamino) stilbazolium butyl sulfonate.



Dye II: (Dihexylamino) stilbazolium butyl sulfonate.



The more hydrophobic dye II due to dihexyl group attached with stilbazolium butyl sulfonate group appears to have stronger interaction with the SDBS micelles. The dye molecules get solubilized in the micelles depending upon their structures as well as surfactant molecules.

One of the important application of surfactants is their ability to solubilize organic additives in the micellar solutions. The aim of present work, was to examine the effect of increasing hydrophobicity upon the solubilization of above dyes in SDBS micelles, and the determination of water-micelle parrition coefficient, K_x, of these dyes by a differential absorption spectroscopic method.

Results and Discussion

The differential absorption spectra of both the aqueous dye solutions at a particular concentration, C_s, in the presence of various concentrations of SDBS. C_s, are shown in Fig. 1. Whereas, the data obtained from these spectra at 25.0°C, is given in Table-1.

Table-1: Relation among differential absorbance ΔA. λ_{max}, and the concentration of SDBS, C_s, in presence of each dye, at 25°C.

(Dimethylamino) stilbazolium butyl sulfonate			(Dihexylamino) stilbazoloium butyl sulfonate		
$C_s \times 10^3$ mol/dm^3	ΔA	λ_{max} nm	$C_s \times 10^3$ mol/dm^3	ΔA	λ_{max} nm
2.0	0.052	482.2	0.5	0.202	484.3
5.0	0.058	482.4	0.8	0.211	484.1
8.0	0.064	482.2	2.0	0.219	484.5
20.0	0.067	482.1	5.0	0.223	484.3
90.0	0.074	482.6	9.0	0.225	484.4
100.0	0.087	482.1	10.0	0.236	484.3
200.0	0.093	482.3			

Concentration of each dye, $C_s = 1.0 \times 10^{-5}$ mol/dm^3.

As the concentration of SDBS, C_s, increases the differential absorption. ΔA, increases for each dye. The increase in ΔA, with surfactant

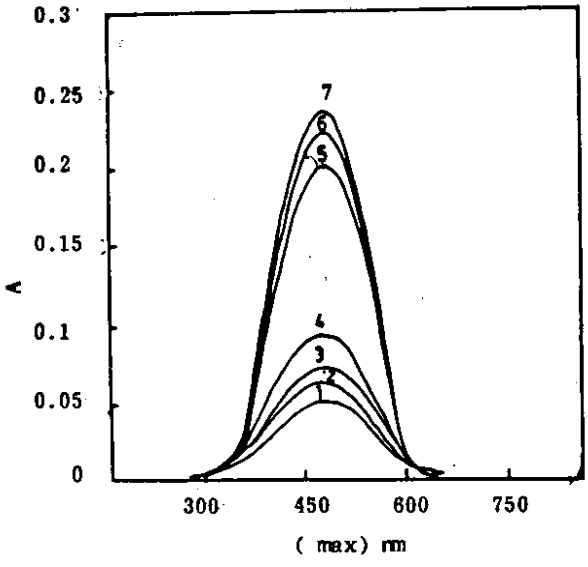


Fig.1: Differential absorption spectra of (Dimethylamino) stilbazolium-butylsulfonate (1, 2,3,4) and (Dihexylamino) stilbazolium butylsulfonate (5,6,7) in SDBS. Conc. of SDBS, Cs* 103 mol/dm^3, (1) 2.0 (2) 8.0 (3) 90.0, (4) 200.0 (5) 0.5 (6) 5.0 (7) 10.0, C_a = 1.0*10^{-5} mol/dm^3.

concentration directly indicates an increase in the amount of solubilised additive (dye) in the surfactant micelles, as observed in other cases [4,5]. The shift of each peak with the increasing surfactant concentration, C_s, can be ignored within the experimental error (± 0.4 nm).

H. Kawamura and M. Manabe [5], suggested that Lambert-Beer's law also holds well for a solubilised additive in the surfactant micelles. They developed an equation for the determination of water-micelle partition coefficient, K, as below.

$$\frac{1}{\Delta A} = \frac{1}{K\,\Delta A_\alpha\,(C_a + C_s^{mo})} + \frac{1}{\Delta A_\alpha}$$

Where ΔA_α represents ΔA at infinity of C_s, K (dm^3/mol) is the water-micelle partition coefficient of an additive. C_s^{mo} is given by the C_s - CMC_o (CMC_o is the critical micelle concentration of a surfactant in water). In our case where hemicyanine dyes were used as additives, K is obtained from the straight line of $1/\Delta A$ against $1/(C_a + C_s^{mo})$. These straight lines are determined by least-squared method of the data, as shown in Fig. 2, of dye I at a certain dye concentration, C_a. The values of water-micelle partition coefficients K (dm^3/mol), K_x (K_x = K n_w/, n_w is the number of moles of water i.e. 55.5 mol/dm^3). ΔG_p^okJ/mol (the standard free energy change of solubilization) of both the dyes are given in Table-2.

Table-2: Values of m_p, K, K_x, and ΔG_p^o of both the dyes at 25°C.

Dye	m_p	K dm^3/mol	K_x	ΔG_o^o kJ/mol
Dimethylamino) stilbazolium butyl sulfonate	2	1660.84	92176.60	-28.322
(Dihexylamino) stilbazolium butyl sulfonate	12	57771.41	3206313.42	-37.115

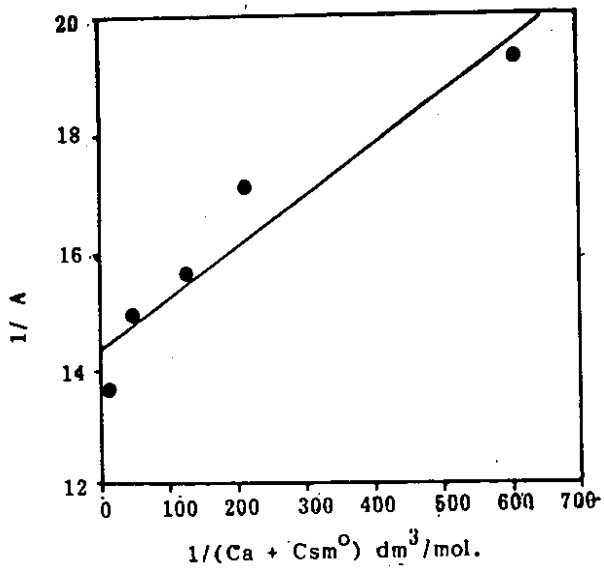


Fig.2: Relation between $1/\Delta A$ and $1/(C_a + C_s^{mo})$ for (Dimethylamino)stilbazolium butylsulfonate, C_a = 1.0x10^{-5} mol/dm^3.

The aminostilbazolium butyl sulfonate group is common in both the dyes, the presence of dialkyl group on the dyes contribute a major role in process of solubilization in SDBS micelles. The less values of K_x, of dye I is due to less solubilization of it into micelles, which in turn depends upon the less hydrophobic dimethyl group. Whereas, more K_x values for dye II suggests, that the more hydrophobic dihexyl group on dye facilitates its solubilization ΔG_p^o, of these dyes from bulk water to micelle is determined from the expression.

$$\Delta G_p^\circ = - RT \ln K_x$$

The low value of ΔG_p° for dye II indicates that its solubilization is more due to its higher hydrophobicity as compared to dye I. The dependence of K_x on the number of carbon atoms in the dialkyl group (m_p) of the two dyes is shown in Fig. 3.

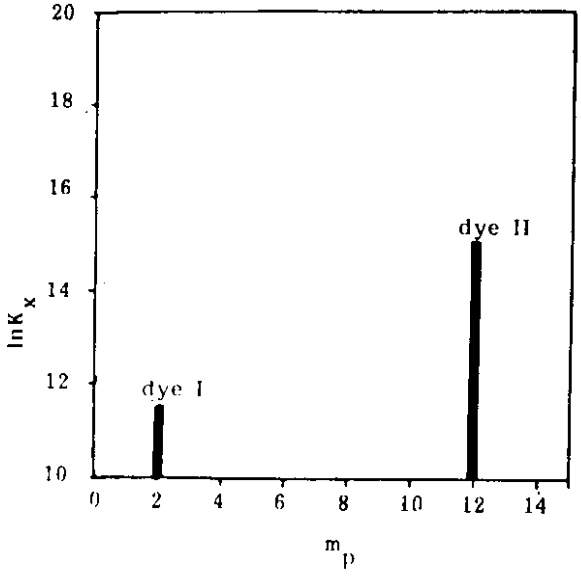


Fig.3: Dependence of $\ln K_x$ on dialkyl chain length (mp) of hemicyanine dyes at 25.0°C.

It is assumed that each dye forms a complex with the surfactant molecules in the bulk of solution prior to the penetration into the micelles [6]. At first, adhesion of dye-surfactant complex to the micelle surface takes place, then dye reorients into the inner hydrophobic portion of the micelles, as observed in case of the anthraquinoid [4,6]. During this reorientation, more hydrophobic dye II makes its way into the interior of micelles more actively. A cationic dye (3,3-diethylthioacarbocyanine) molecules play a very important role in the formation and stabilization of dye aggregates in the micelles [7] and its is also true in the case of our hemicyanine dyes.

Experimental

Materials

Solid sodium dodecyl benzene sulfonate (SDBS), a product of Fluka was of analytical grade and used without further purification. The two hemicyanine dyes were in solid form and were obtained from Dr. P. Fromherz's Lab. in Ulm. Germany.

Procedure

An aqueous Hemicyanine dye solution was prepared by dissolving the solid dye in 0.5 ml methanol which was then diluted to 500 ml stock solution with deionized water to obtain the required dye concentration (C_a) of 1×10^{-5} mol/dm^3. Out of this stock solution one portion was used as reference for differential absorption measurement while the rest was used as solvent for SDBS solution of various concentrations. Differential absorption spectra were taken on a Shimadzu double-beam UV-285 type recording spectrophotometer at 25°C. Differential absorbance (ΔA) against λ_{max} of each SDBS solution was measured by using two cuvettes, one filled with dye solution as reference and the other with the sample solutions. The dye concentration was kept constant as shown in Fig. 1. The temperature was maintained within ± 0.1°C by using a thermostat.

Critical micelle concentration (CMC_O) of SDBS in water was determined by a point of intersection of two straight lines obtained from a plot of specific conductance VS concentration of SDBS. Specific conductance of aqueous SDBS solutions without dye was measured on Microprocessor conductivity meter (WTW), LF 2000/C, Germany at 25.0 ± 0.01 °C. CMC_O of SDBS was $3.72 \pm 0.02\ 10^{-4}$ mol/dm^3 at 25.0 °C.

Acknowledgement

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