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Interaction of ketocyanine dyes with cationic, anionic and neutral micelles

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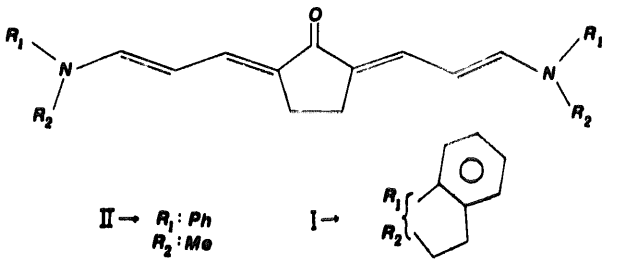
Abstract

Interaction of ketocyanine dyes with cationic (CTAB), anionic (SDS) and neutral (Triton X-100) micelles has been studied by monitoring the polarity-sensitive absorption and fluorescence band of the solute. The position of equilibrium between the bare form of the dye (S_0 state) and its hydrogen-bonded complex with water is modified by the micellar medium, the percentage of the hydrogen-bonded species being maximum in SDS, while it is minimum in CTAB. The negative carbonyl centre of the dye avoids the anionic micelle (SDS) and is effectively hydrogen bonded by water. Fluorescence band maximum provides the micropolarity of the micelle–water interface and the local dielectric constant and $E_T(30)$ value determined agree well with the value for the micellar medium reported in the literature. The possible orientation of the dye in the proximity of the micelle has also been discussed.

Keywords: Ketocyanine dyes; Cationic micelles; Anionic micelles; Neutral micelles

1. Introduction

Fluorescent probes are used extensively for studying local parameters in chemical and biological systems [1]. A most important criterion in the choice of a probe is its sensitivity towards a particular property of the microenvironment where the probe is located. Ketocyanine dyes provide an interesting system for probing the micropolarity [2,3] since the absorption and the emission spectra of this class of compounds show solvent sensitivity. In recent communications [4–6] we have studied extensively the absorption and fluorescence characteristics of ketocyanine dyes in various homogeneous media. It has been found that the dye interacts with protic solvents through hydrogen bond donation (HBD), the extent of interaction being greater in the S_1 state. This property makes the dye a good fluorescent probe for studying the HBD interaction. Compared with a homogeneous medium (pure or mixed solvents), solutions of organized assemblies possess many unique properties [7]. Of the different self-organized systems, the micellar systems, owing to their importance as model systems mimicking biomembranes, have been subjected to several investigations [8–13]. The present paper aims at studying the spectral features of ketocyanine dyes in micellar media. The main objective is to extract the information regarding the interaction of these dyes with the micelles. Both the absorption and the emission spectra of two ketocyanine dyes (I and II (Scheme 1)) have been studied in aqueous media containing cationic (CTAB), anionic (SDS) and neutral (Triton X-100) micelles. The results have been interpreted using the similar studies of the dyes in several mixed solvents.



Scheme 1.

2. Experimental details

Dyes I and II have been prepared by methods described in the literature [2]. The surfactants, namely CTAB, SDS and Triton X-100 (Aldrich), were used as received. The water used was triply distilled. The absorption spectra were recorded in a Hitachi 32100 spectrophotometer and the emis-

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sion studies were done on a Hitachi F-4010 spectrofluorometer equipped with a 150 W xenon lamp. Freshly prepared solutions were used for each measurement.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the two dyes in the micellar environment at 298 K are shown in Fig. 1. For all the micellar systems, two bands appear for both the dyes, but their relative intensities are different. Our earlier studies in homogeneous solvents [4,5] indicated that, in a solution containing protic solvents, ketocyanine dyes exist in equilibrium between an uncomplexed species and a hydrogen-bonded solvated species. The hydrogen-bonded species in ethanol shows absorption at around 550 nm for dye I and 520 nm for dye II at 298 K. The position of maximum absorption for the uncomplexed species varies with the nature of the solvent and for *n*-hexane it is around 460 nm for dye I and 440 nm for dye II at 298 K. The absorption spectra of dye I in a mixed solvents of cetyl alcohol (CTOH) and tetrachloromethane also show an isosbestic point (Fig. 2), indicating that two species are present in this solution. Thus the two bands appearing in the micellar medium correspond to a bare dye molecule and a hydrogen-bonded species. The position of equilibrium between the two species, however, depends on whether the micelle is cationic, anionic or neutral. It appears from Fig. 1 that the percentage

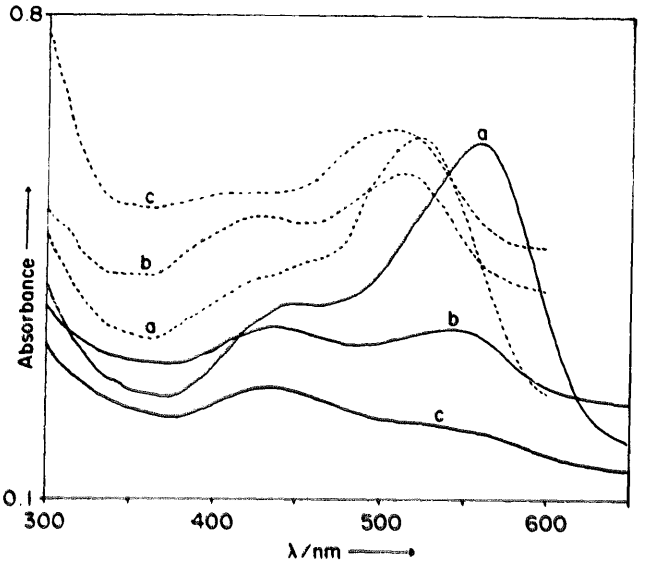

Fig. 1. Absorption spectra of dye I (——) and dye II (– – –) in different micellar media: curves a, SDS; curves b, CTAB; curves c, Triton X-100. The concentration of the dyes are in the range 10^{-5}–10^{-6} mol dm^{-3}.

of hydrogen-bonded species is maximum in SDS while it is minimum in CTAB. The result is intelligible in view of the fact that the hydrogen bonding centre, i.e. the carbonyl oxygen atom, which is a negative centre is repelled by the anionic micelle (SDS) and thus exposed to water phase, leading to a greater hydrogen bonding.

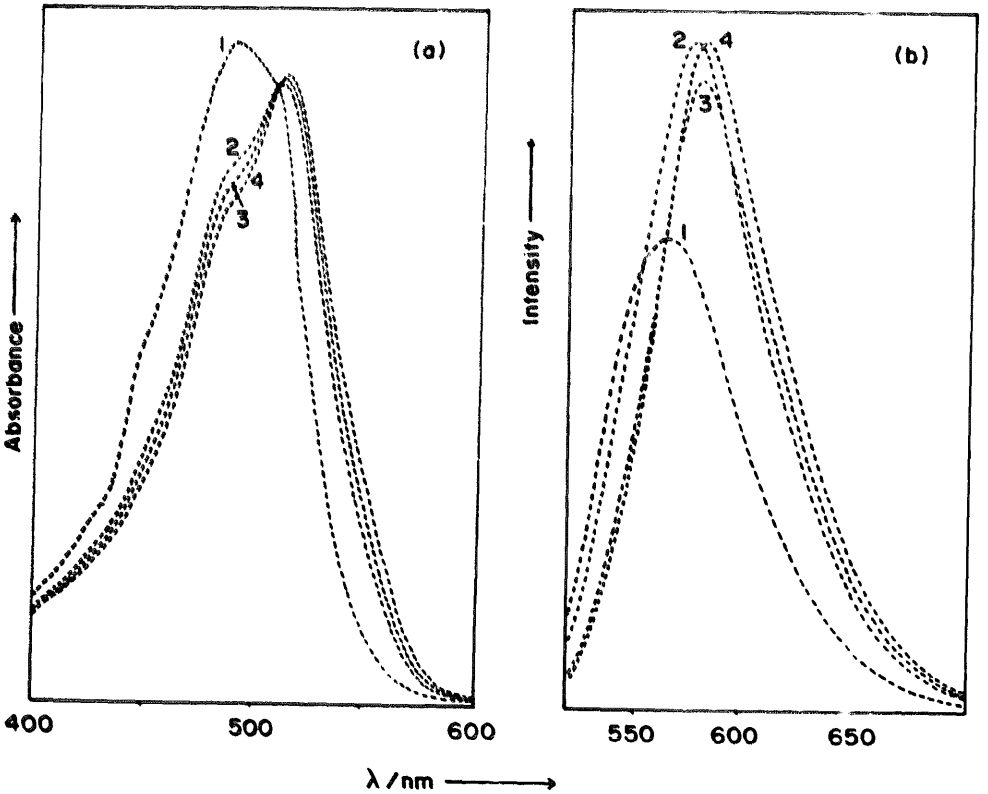

Fig. 2. (a) Absorption spectrum and (b) fluorescence spectrum of dye I in CTOH + CCl_4 medium. The concentration of CTOH increases in the order curve 1 > curve 2 > curve 3 > curve 4.

3.2. Fluorescence spectrum

The fluorescence spectra of the dyes in the three surfactant solution (above CMC) at 298 K are shown in Fig. 3. Unlike the absorption the fluorescence is characterized by one band, the position of the band maximum being dependent on the nature of the micelles. The maximum energy of transition is in the order CTAB > Triton X-100 > SDS. The hydrogen-bonded complexed solute is the emitting species as evidenced by the fact that the excitation spectra for all the micellar systems show a maximum at a wavelength corresponding to the maximum of hydrogen-bonded species. We have discussed in earlier communications [4–6] the fact that the fluorescence observed for ketocyanine dyes originates from an intramolecular charge transfer (ICT) transition and the position of the fluorescence maximum in a homogeneous medium is governed by the micropolarity of the environment. For a protic solvent the maximum energy of transition is largely determined by the HBD interactions between the solvent and the carbonyl oxygen atom in the excited state. The greater the hydrogen-bonding ability, the lower is the energy of transition. Thus the HBD interaction in the micellar system increases in the order CTAB > Triton X-100 > SDS. The hydrogen-bonding interaction of the medium is also reflected in the Stokes shift for the dyes. It has been observed that the protic solvents are characterized by a larger Stokes shift. The magnitude of the Stokes shift is about 2700 cm^{-1} for dye I and about 2300 cm^{-1} for dye II in SDS, while it is about 2300 cm^{-1} and about 1900 cm^{-1} in CTAB.

For a CTOH + CCl_4 mixture the fluorescence band maximum changes continuously to a higher value as the percentage of CCl_4 in the mixture decreases (Fig. 2(b)). This is consistent with our earlier observation [4–6] that the emission band maximum is sensitive towards a change in the local polarity around the dye in a binary mixed solvent.

It is interesting to note that the ketocyanine dyes are insoluble in water in spite of the fact that the hydrogen-bonded interaction with the carbonyl oxygen atom is greatest for water [14]. This is perhaps due to the presence of two large hydrophobic rings present in dye I and dye II. However, the dyes are soluble in the presence of the surfactants (SDS having the largest effect) and above the CMC values the amount of solute solubilized is proportional to the surfactant concentration (Fig. 4). Thus the solubilization in the micellar systems points to a dye–micellar interaction. The dyes are found to be insoluble in *n*-hexane. The possibility that the dye is incorporated in the interior of the micelles which resembles hydrocarbon-like solvents may thus be ruled out

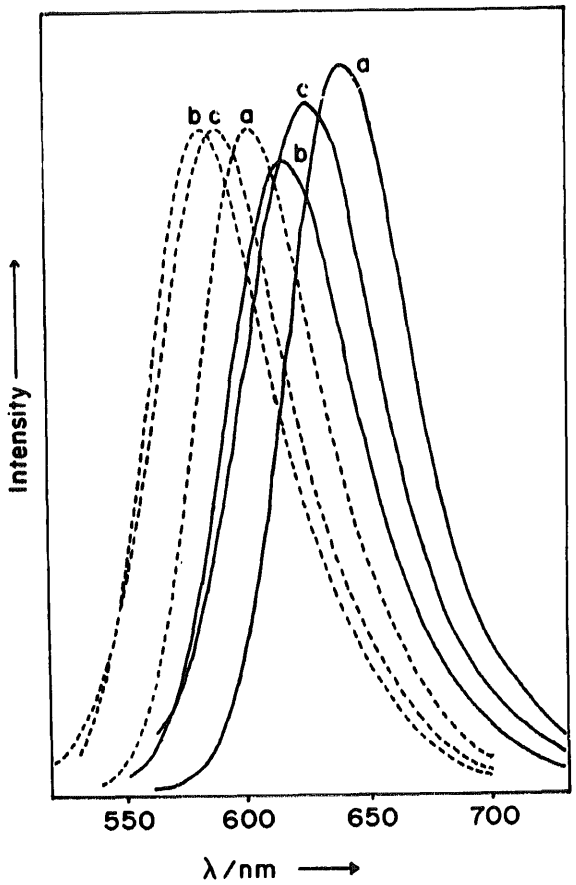

Fig. 3. Fluorescence spectra of dye I (——) and dye II (– – –) in different micellar media: curves a, SDS; curves b, CTAB; curves c, Triton X-100.

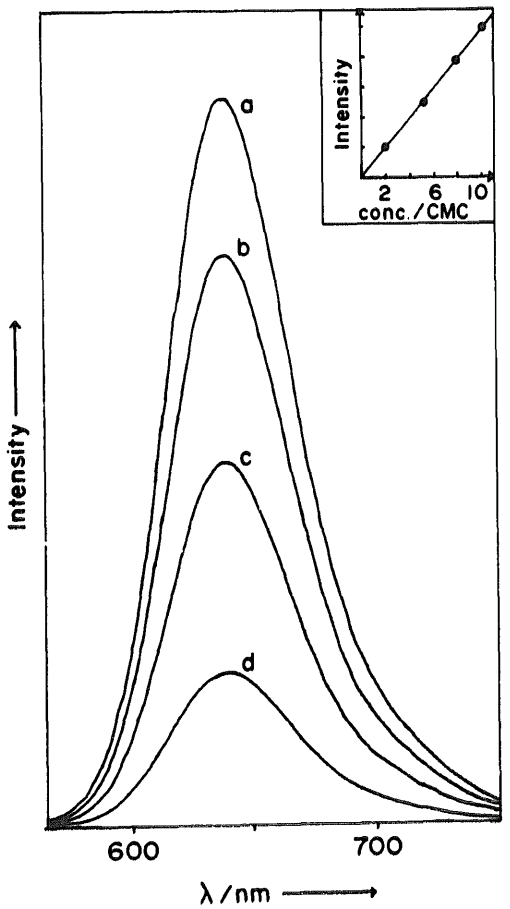

Fig. 4. Fluorescence spectrum of dye I and SDS micellar medium as a function of micelle concentration: curve a, 10 CMC; curve b, 8 CMC; curve c, 50 CMC; curve d, 2 CMC. The plot of fluorescence intensity vs. micelle concentration is shown in the inset.

and the dye molecules may be supposed to be located at the micelle–water interface.

3.3. Micropolarity of the interface

For the micellar systems studied, the estimates of local dielectric constant and micropolarity in the $E_T(30)$ scale may also be obtained. For this the maximum energy of fluorescence of the dyes in alcohols or ethanol + water mixture were measured and plotted against the respective dielectric constant or $E_T(30)$ values. From the curves the local values of dielectric constant or $E_T(30)$ for the micellar systems may be obtained. Alcohols and ethanol + water systems were chosen because these are better model solvents in view of the fact that, apart from the head groups and counter ion, only water and alkyl chains contribute to the surface polarity of the aqueous micelles [15]. The microenvironmental parameters have been listed in Table 1. The values of the microenvironmental parameters determined agree well with the values reported in the literature [9,15], where the $E_T(30)$ values have been directly determined using the indicator dye for $E_T(30)$ scale. The observed values of the micropolarities also indicate that the dye is located at the micelle–water interface.

The negative charge density on the carbonyl oxygen of the dye will be involved in the electrostatic interaction with the polar head groups. Besides this, hydrophobic interaction of the hydrocarbon-like wings of the dye with the micelles also plays a part, as reported by other workers for different dyes [16]. In the CTAB micelle the positively charge head groups will attract the negative charge density of the carbonyl oxygen of the dye; thus the dye will be transferred to a more hydrophobic environment. This interaction will increase when the dye is in the S_1 state and the extent of hydrogen-bonded interaction with water will be diminished, leading to an increase in the transition energy of fluorescence. In the presence of benzoate ions as counter-anions in the CTAB micelle, quenching of fluorescence is observed, while the fluorescence maximum remains almost unaltered. It is to be noted that bromide ions, a fairly effective quencher, shows no quenching effect. Possibly the bromide ions in the Gouy–Chapman layer are shielded from the carbonyl group owing to solvation by water, while the benzoate ion containing a hydrocarbon-like part will not be effectively shielded from the carbonyl group. Moreover, benzoate ions, being bulkier and containing a hydrophobic part, decrease the aggregation number of CTAB. Thus benzoate ions will be able to penetrate somewhat inside the micelles, causing quenching.

In the SDS micelle, on the contrary, the negatively charged head groups will repel the negative charge density on the carbonyl oxygen; thus the chromophoric part of the dye will be in a more hydrophilic environment and will be more effectively hydrogen bonded by water. This is reflected in the observation that the fluorescence maximum of the dyes in SDS evolution is very close to that observed in pure water. The non-ionic surfactant Triton X-100 consists of bulky phenyl head groups and a long polyoxyethylene chain which terminates in an –OH group. The fluorescence maximum in a Triton X-100 micelle appeared around the same region as in ethanol, indicating that the interaction of the dye with the terminal –OH groups is important.

Table 1
Microenvironmental parameters for dye I and dye II in ordered media

	Dye I		Dye II	
	ϵ	$E_T(30)$	ϵ	$E_T(30)$
CTAB	10.0	50.1	10.0	50.2
SDS	64.5	57.2	62.2	56.0
Triton X-100	27.0	52.4	24.0	52.2

4. Conclusion

The present work demonstrates that a study of the absorption and fluorescence characteristics of the ketocyanine dye may provide information regarding the microenvironmental properties of the micelle–water interphase in aqueous micelles.

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