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Time-resolved fluorescence studies of aminostyryl pyridinium dyes in organic solvents and surfactant solutions

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Abstract

Absorption, fluorescence emission spectra and fluorescence lifetimes of N-alkyl-4-(p-N,N-dimethyl aminostyryl) pyridinium dyes of varying lengths of alkyl chain have been measured in different organic solvents (protic, dipolar aprotic and aprotic) and in different surfactant solutions. The spectra for the dyes are similar in a single solvent but vary with solvent type. The Stokes shift for the dye does not vary with the solvent parameter as predicted by Lippert–Mataga equation. The fluorescence decay of the dyes shows two lifetimes in organic solvents except in a few solvents where a single or three lifetimes were obtained. The lifetime results are interpreted in terms of emission from cis and quinoid (or intramolecular charge transfer, ICT) forms of the dye in the excited state. The spectra and fluorescence lifetime results for the cis isomer (synthesized as a stable compound) in organic solvents confirmed the coexistence of multiple species. In surfactant solutions, the spectra and fluorescence lifetimes of the dyes depend upon the length of the alkyl chain of the dye and the concentration of the surfactant, namely, premicellar or post micellar. Dye–surfactant complexes were identified in a few cases in SDS and CTAB premicellar solutions. TX-100 surfactant is found to stabilize the cis isomer for all the dyes, whereas both SDS and CTAB surfactants stabilize the trans isomer predominantly.

Keywords: Micelles; Quinoid isomer; Charge transfer state; Dye–solvent complex; Aggregates

1. Introduction

Aminostyryl pyridinium (ASP) dyes have been widely used as fluorescent probes in the micellar studies [1,2] and they are known for their voltage-sensitive fluorescence in lipid membranes [3]. Several mechanisms have been proposed for the voltage sensitivity of fluorescent aminostyryl dyes for the visualization of voltage transients in membrane preparations [4–6], such as, electrochromism, dye reorientation, and formation of twisted intramolecular charge transfer (TICT) state [7–9]. Recently, the molecular aggregates that are formed by the noncovalent and/or ionic interactions between organic molecules and surfactant ions were found to have special structural and optical properties [10–12]. In this paper we present the spectroscopic observations on styryl dyes of increasing chain length attached to the pyridine moiety in organic solvents and in surfactant solutions. One of the main aims of this

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study is to understand the photophysics of these important dyes and how the microheterogeneous media such as micelles affect their photophysics.

2. Experimental

2.1. Materials and methods

N-Alkyl-4-(p-N,N-dimethylamino styryl) pyridinium bromides were prepared by the method reported earlier [13,14]. The structure is shown in Fig. 1. 4-Methyl pyridine was quaternized with alkyl bromide of varying chain length and was then condensed with p-N,N-dimethylamino benzaldehyde in ethanol in the presence of 2–3 drops of piperidine. The reaction mixture was concentrated by evaporating ethanol. Cooling on ice separated red solid. The product was crystallized from absolute ethanol. Purity of the compound was checked by TLC (silica gel, eluent mixture of methanol–acetone, 3 : 1 v/v) and the extinction coefficient after each crystallization. Cis isomer of N-alkyl-4-(p-N,N-dimethyl aminostyryl) pyridinium bromide was synthesized by the method reported elsewhere [15]. Generally, 2–3 crystallization were required for obtaining a constant value of molecular extinction coefficient. The dyes are referred to as C_n according to the number (n) of carbon atoms in the alkyl chain. Sodium dodecyl sulphate (SDS) (purchased from Sisco Chem, Spectroscopic grade) was recrystallized twice from ethanol and dried in vacuo over P_2O_5. Cetyl trimethyl ammonium bromide (CTAB) (Sisco Chem, Spectroscopic grade) was purified by recrystallization twice from methanol–acetone mixture (3 : 1 v/v) and dried over P_2O_5. Triton X-100 (Qualigen, spectroscopic grade) was used as received. Triple distilled water was used throughout the experiment. Solvents used were either of spectroscopic grade or were purified by the method reported earlier [16].

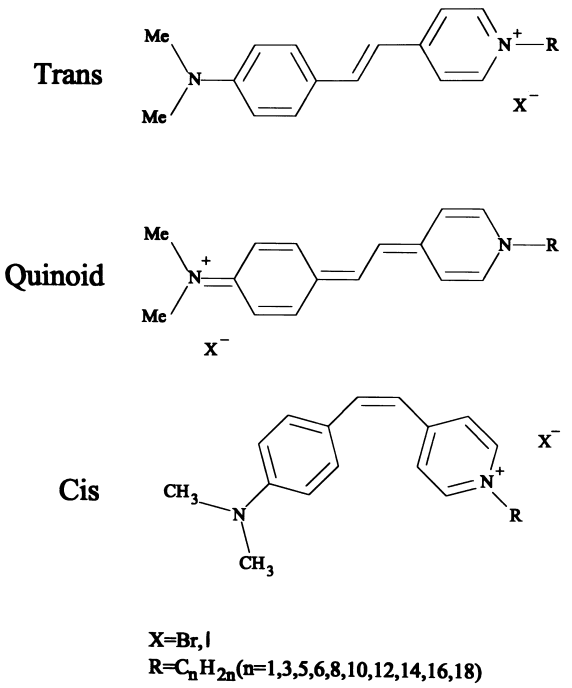

Fig. 1. Molecular structure of the aminostyryl pyridinium dye molecule. The trans, quinoid and cis forms of the dye are shown. The quinoid form is also the intramolecular charge transfer state (ICT). R is the n-alkyl group.

2.2. Spectroscopic measurements

A concentrated (ca. 1 mM) stock solution was prepared separately for each dye by dissolving required amount of the dye in methanol. The solution for spectral measurement was prepared by adding 0.1 ml of the above stock solution to a 5-ml volumetric flask containing freshly prepared solution of the surfactant in triply distilled water. Aliquots (3 ml) of these solutions were added to quartz cuvettes maintained at 25°C. Absorption spectra were obtained on Shimadzu 160 spectrophotometer and fluorescence emission spectra were obtained on a Shimadzu RF-5000 spectrofluorophotometer. The time-resolved fluorescence decay measurements were made using a high-repetition rate picosecond laser coupled to a time-correlated single photon counting spectrometer described elsewhere [17] currently using a microchannel plate photomultiplier (Hamamatsu 2809) and personal computer for data acquisition and analysis. The sample was excited at 570 nm by vertically polarized laser pulses and the emission at 590 or 600 nm was collected with an emission polarizer oriented at the magic angle of 54.7° with respect to the excitation polarization. The

full-width at half-maximum of the instrument response function was approximately 200 ps. Typical count rate for fluorescence decay measurements was 4000–5000/s ($\sim 0.5\%$ of the excitation rate) and the typical peak count was $5–10 \times 10^3$. The fluorescence decays were fitted to one, two or three exponentials, as necessary [17]. A three exponential function was considered to be meaningful only if the goodness-of-fit parameters (χ^2 and distribution of weighted residuals, see Fig. 2) are significant improvements to those obtained when the same data set was subjected to a two exponential fit. It was also noted that in all cases where three exponential fit was required the three lifetimes were differed from each other by a factor 3–5 and a two exponential fit was not possible. The short lifetime component > 30 ps can be detected by deconvolution analysis especially if the amplitude is significant [12,17]. The average lifetime, τ_{av} is calculated as $\tau_{av} = (\Sigma_i \alpha_i \tau_i)/(\Sigma_i \alpha_i)$, where α_i and τ_i are the amplitudes and lifetimes.

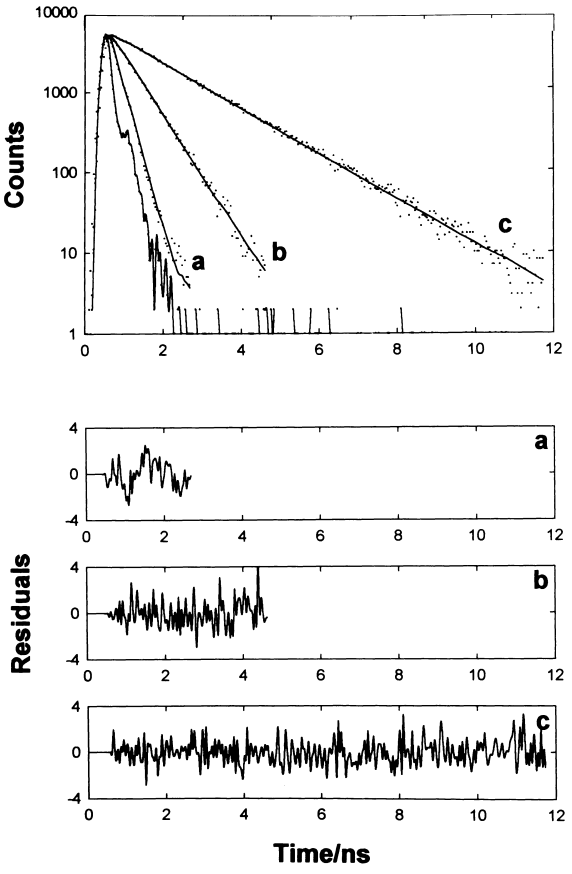

Fig. 2. Fluorescence decays of C_3 dye in: (a) n-butanol; (b) methylene chloride; and (c) chloroform. The excitation function is also shown. The smooth curves passing through the data are good fits to a single exponential (methylene chloride) and two exponentials (butanol and chloroform). The distribution of weighted residuals are shown in the bottom panels.

3. Results

3.1. Fluorescence in organic solvents

Absorption and fluorescence emission spectra of the 10 dyes (Fig. 1, $n = 1, 3, 5, 6, 8, 10, 12, 14, 16$ and 18) were measured in various organic solvents. The spectra of the 10 dyes are very similar to each other in a single solvent except water in which the solubility of some dyes with long alkyl chains is poor. The spectral peak positions and Stokes shift showed a variation of less than 5 nm in a single solvent indicating that the electronic transition of the aminostyryl pyridinium chromophore is not perturbed significantly by the length of the alkyl chain length attached to the pyridinium nitrogen. There was however a significant variation in the spectral peak positions and Stokes shift for the dye in different solvents. Table 1 shows the typical values of the spectral peak positions, molar extinction coefficient, relative fluorescence intensities and Stokes shift for one dye, namely C_3. The results for other dyes were similar. The fluorescence decays of three representative dyes of different alkyl chain lengths ($n = 3$, 10 and 16) were measured in different solvents. The fluorescence decays were two exponentials in most solvents. In a few solvents however the decay is a single exponential or a sum of three exponentials. Fig. 2 shows the fluorescence decays of C_3 dye in butanol, methylene chloride and chloroform. The fluorescence decays were fitted to two exponentials (butanol and chloroform) or a single exponential (methylene chloride) to obtain good fits (indicated by the randomness of weighted residuals in Fig. 2, bottom panels). The lifetime results are similar for other dyes. The results are summarized in Table 2 for one dye, C_{16}. The lifetime results of these dyes in all the solvents (and also in surfactant solutions,

Table 1
Absorption and fluorescence emission maxima, and Stokes shift values of C_3 dye in various solvents. ([dye] = 0.02 mM, slit width = 5 nm)

Solvent	Δf[a]	λ_{max}/nm (log ε)	λ_{em}/nm (rel. int.)	Stokes shift (cm^{-1})
MeOH	0.309	479 (4.74)	579 (1.0)	3605
EtOH	0.289	484 (4.74)	576 (2.9)	3300
Propanol-2	0.273	485 (4.73)	571 (6.2)	3105
Butanol-1	0.275	490 (4.80)	576 (8.7)	3047
Butanol-2	0.261	489 (4.78)	573 (10.2)	2998
Isobutanol	0.243	491 (4.75)	573 (9.9)	2915
Cyclohexanol	0.235	492 (4.72)	571 (27.5)	2812
Ethylene glycol	0.275	482 (4.70)	582 (4.5)	3565
$CHCl_3$	0.148	496 (4.78)	560 (17.3)	2304
CH_2Cl_2	0.217	513 (–)	560 (~ 8.0)	1636
Acetonitrile	0.305	474 (4.71)	555(sh), 584 (0.2)	3974
Acetone	0.284	476 (4.72)	586 (0.66)	3944
DMF	0.274	474 (4.68)	587 (1.0)	4062
DMSO	0.263	476 (4.68)	589 (1.6)	4030
DMA	–	474 (4.69)	587 (1.6)	4061
Dioxane	0.020	463 (4.70)	557 (15.8)	3644
Pyridine	0.214	494 (4.71)	589 (2.6)	3265
Benzene	0.003	477 (4.80)	552 (10)	2848

[a] $\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$, where ε is the dielectric constant and n is the refractive index.

Table 2
Fluorescence lifetimes of C_{16} dye in organic solvents (with MeOH 2% by volume)

Solvents	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
Water	0.05	0.56	2.07	0.961	0.026	0.013	1.29	0.09
Methanol	0.09	–	2.23	0.957	–	0.043	1.05	0.19
$CHCl_3$	0.35	–	1.63	0.116	–	0.884	0.95	1.48
CH_2Cl_2	–	0.59	–	–	1.000	–	0.86	0.59
Acetone	<0.03	–	2.11	0.999	–	0.001	1.09	<0.03
Acetonitrile	<0.03	–	1.79	0.999	–	0.001	1.58	<0.03
Dioxane	0.17	0.62	2.20	0.960	0.029	0.010	1.10	0.21
DMF	0.05	–	3.48	0.976	–	0.024	1.21	0.13
DMSO	0.12	–	–	1.000	–	–	1.10	0.12
Benzene	0.11	–	1.84	0.997	–	0.003	1.06	0.11
Toluene	0.12	–	1.27	0.992	–	0.008	1.07	0.13
Butanol-1	0.21	–	–	1.000	–	–	0.93	0.21
1,2-Glycol	0.23	0.52	–	0.930	0.070	–	0.92	0.25
Glycerol	0.49	–	1.53	0.279	–	0.721	1.02	1.24

see below) fall in one of three ranges: short lifetime ($\tau_1 < 0.3$ ns), middle lifetime ($\tau_2 = 0.4$–0.8 ns) or long lifetime ($\tau_3 > 1$ ns). Hence, the lifetime results in all the tables are arranged in that order.

3.2. Fluorescence in surfactant solutions

The dyes used in this study are amphiphilic molecules containing an alkyl chain of varying length and a cationic chromophore. The interaction of the amphiphilic cationic dye with surfactant molecules and the type of dye-surfactant aggregate formed will depend upon various factors: concentration of the surfactant, especially pre- and post-micellar regimes, type of surfactant (cationic, anionic or neutral), and the alkyl chain length in the dye molecule. Of particular interest is the possibility of formation of special dye

aggregates such as J- and H-aggregates in surfactant solutions as in the case of water soluble porphyrins [12]. The formation of dye–surfactant aggregates is facilitated by noncovalent interactions between the dye and surfactant molecules. Steady-state and time-resolved fluorescence experiments were carried out for the 10 dyes in SDS, CTAB and TX surfactant solutions. The results are summarized below.

3.2.1. SDS

SDS is an anionic surfactant and one expects coulombic interaction to be a significant one for the formation of dye–surfactant aggregate. The absorption spectra of the 10 dyes were recorded at different concentrations of the surfactant. The characteristics of the spectra varied systematically with the alkyl chain length of the dye. Fig. 3 shows the absorption spectra of the dye for different concentrations of the surfactant: 0.02, 2, 4 and 20 mM for C_3, C_8 and C_{16} dyes. The dye concentration was maintained at 0.02 mM for all spectra. The cmc for SDS is 8 mM [18] and the spectra shown are for premicellar and post-micellar concentrations. There is a noticeable red shift in the absorption spectra of C_3 and C_8 dyes in pre- and post-micellar regimes. This feature is to be expected for all hydrophobic organic molecules because the dye in the pre-micellar regime is more exposed to the aqueous solvent than in post-micellar regime where the dye is fully pulled towards the hydrophobic region of the micelle. An interesting observation in SDS solutions is the formation of dye–surfactant complexes when the surfactant concentration is less than critical micelle concentration (cmc). In some cases, the formation of a dye–surfactant complex leads to turbidity indicating a phase separation [19]. For example, a noticeable dye–surfactant complex is formed in the case of C_3 (Fig. 3A, curve b) at 2 mM, and C_{16} (Fig. 3C, curve a) at 0.02 mM. In the case of C_{16}, the absorption spectrum of the complex is blue-shifted and the spectral width is narrow, compared to the spectrum in organic solvents or in micellar solution.

Time-resolved fluorescence decay measurements were made for all 10 dyes in two concentrations of the surfactant: 2 and 20 mM. The dye concentration was less than 5 μM in all cases. The fluorescence decays were fitted to a sum of two or three exponentials and the results are tabulated in Tables 3 and 4. The lifetime results are tabulated as short (τ_1), medium (τ_2) and long (τ_3) lifetimes. At low surfactant concentration (2 mM) all the three lifetimes were observed but when in micellar concentration the short lifetime (τ_1) is predominant.

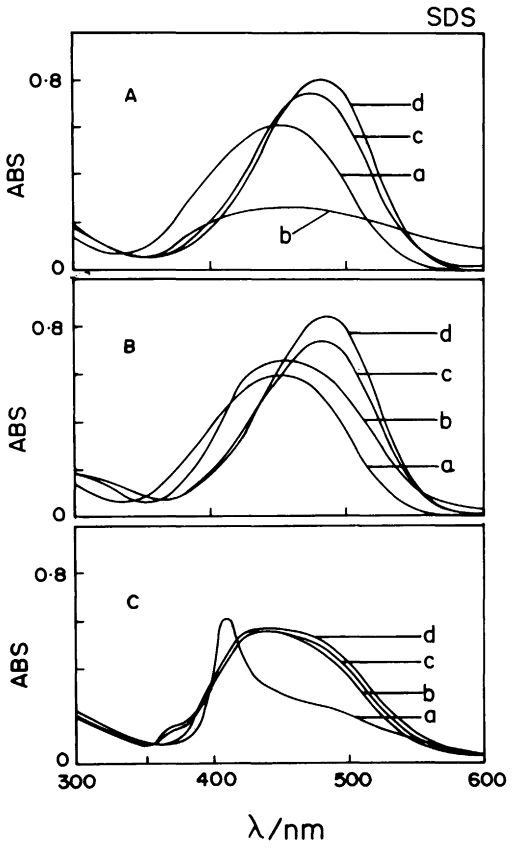

Fig. 3. Absorption spectra for: (A) C_3; (B) C_8; and (C) C_{16} dyes in SDS solutions for different concentrations: (a) 0.02; (b) 2; (c) 4; and (d) 20 mM.

3.2.2. CTAB

CTAB is a cationic surfactant and the cmc value is 0.92 mM [18]. As in the case of SDS, the interaction of the dye (0.02 mM) with the surfactant varies systematically with the concentration of the surfactant and the length of the alkyl chain attached to the dye. Fig. 4 shows the spectra

Table 3
Fluorescence lifetime results of various C_n dyes in SDS solution ([SDS] = 2 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.05	0.22	1.86	0.925	0.067	0.008	0.98	0.07
C_3	0.04	0.14	1.71	0.813	0.185	0.001	1.22	0.06
C_5	0.13	0.29	1.75	0.88	0.096	0.024	0.99	0.19
C_6	0.13	0.40	1.88	0.908	0.072	0.021	1.01	0.19
C_8	0.11	0.69	2.20	0.907	0.064	0.029	1.08	0.20
C_{10}	0.15	0.69	2.04	0.916	0.052	0.032	0.97	0.24
C_{12}	0.13	0.74	2.20	0.875	0.084	0.042	0.88	0.26
C_{14}	0.14	0.58	2.11	0.837	0.121	0.046	1.19	0.29
C_{16}	0.14	0.63	2.31	0.897	0.077	0.026	0.98	0.23
C_{18}	0.15	0.60	2.35	0.873	0.095	0.032	1.02	0.27

Table 4
Fluorescence lifetime results of various C_n dyes in SDS solution ([SDS] = 20 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.17	–	1.65	0.999	–	0.001	0.93	0.17
C_3	0.19	0.48	–	0.993	0.007	–	1.00	0.19
C_5	0.22	–	2.00	0.998	–	0.002	0.91	0.23
C_6	0.23	0.24	–	0.993	0.007	–	1.00	0.23
C_8	0.22	0.66	–	0.994	0.006	–	1.10	0.23
C_{10}	0.24	–	1.01	0.997	–	0.003	1.23	0.24
C_{12}	0.22	–	1.15	0.993	–	0.007	0.91	0.23
C_{14}	0.23	0.56	2.12	0.949	0.036	0.015	0.91	0.27
C_{16}	0.19	0.43	2.04	0.834	0.12	0.046	1.15	0.30
C_{18}	0.17	0.76	2.70	0.838	0.112	0.05	0.81	0.36

for three dyes (C_8, C_{12} and C_{16}) at premicellar surfactant concentrations (0.02, 0.5 mM) and micellar concentrations (4 and 10 mM). The spectra for all the dyes are similar when the surfactant concentration is 10 mM, well above cmc. For those dyes with shorter alkyl chain ($n<10$) the spectral changes are similar to that as shown in Fig. 4A. The spectrum shifts to the red as the surfactant concentration increases to micellar regime. For dyes with longer alkyl chain ($n > 12$) one observes evidence for new structures of dye–surfactant aggregates. For example, the solution of C_{12} dye becomes turbid when CTAB concentration is about 1 mM and the absorbence decreases substantially (Fig. 4B, curve b). The effect is more pronounced in C_{16} dye (Fig. 4C) where the dye–surfactant aggregate has a narrow peak at 400 nm when the surfactant concentration is 1–3 mM.

Time-resolved fluorescence decays of the 10 dyes were measured in CTAB solutions for two concentrations (0.8 and 10 mM) and the results of fitting the decays to two or three exponentials are shown in Tables 5 and 6. All the lifetime results could be tabulated as short (τ_1), medium (τ_2) and long (τ_3) lifetimes. A significant deviation from the general trend was observed for C_{12}, C_{14}, C_{16} and C_{18} dyes at the low surfactant concentration. The long lifetime component is significantly higher in magnitude compared to the dyes with shorter chains and also the middle lifetime with significant fraction appears in these cases.

3.2.3. TX

Triton-X100 is a neutral surfactant and the cmc is 0.26 mM [18]. The absorption spectra for the 10 dye molecules in TX at different concentrations were similar (Fig. 5). There were no unusual spectral changes for any dye in TX solutions as was observed in SDS or CTAB solutions.

The fluorescence lifetime results of the 10 dyes in TX solutions for two concentrations (0.6 and 11.88 mM) are given in Tables 7 and 8. The most significant observation in TX surfactant solutions is the higher fraction of the medium lifetime (τ_2) compared to the case of SDS and CTAB surfactants.

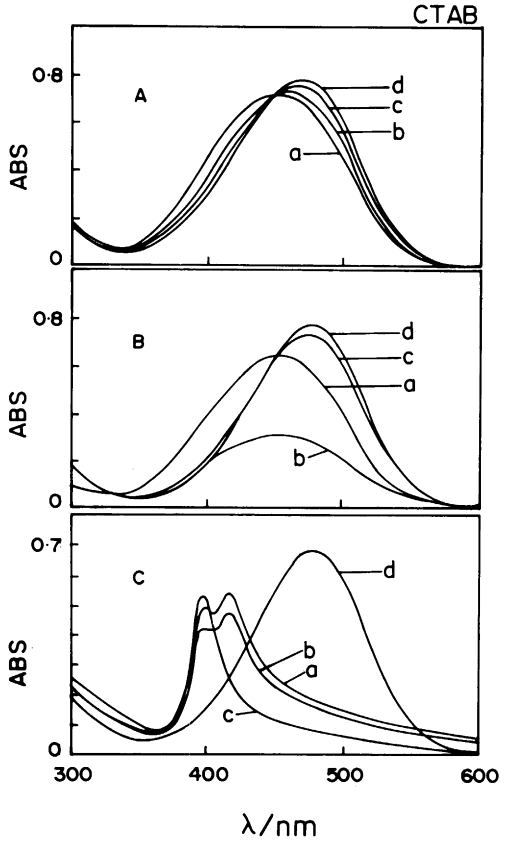

Fig. 4. Absorption spectra for: (A) C_8; (B) C_{12}; and (C) C_{16} dyes in CTAB solutions for different concentrations: (a) 0.02; (b) 0.5; (c) 4; and (d) 10 mM.

3.2.4. Fluorescence of the cis isomer

The absorption and emission spectra of the cis isomer of the C_1 dye was studied in several solvents. The absorption spectra of the cis isomer showed a blue-shifted band (423–462 nm due to n–π^* transition) compared to the trans isomer and an additional band in the 320–340 nm region due to π–π^* transition. The formation of two separate bands in cis isomer is due to the distortion of symmetry of the dye. The fluorescence emission was observed at $\sim$ 550 nm, which is again blue-shifted to that of the trans isomer. The absorption and emission maxima of the cis isomer are given in Table 9 and compared with those of the trans isomer. The fluorescence lifetime results of the cis and trans isomer in different organic solvents are also given in Table 10.

4. Discussions

4.1. Structure of the dye in organic solvents

An important question to be addressed in interpreting the fluorescence spectroscopic results in organic solvents is the identification of the structure or structures for the dye in different solvents. Fluorescent molecules with rigid ring structures (like anthracene) retain the same structure in ground and excited state in any organic

Table 5
Fluorescence lifetime results of various C_n dyes in CTAB solution ([CTAB] = 0.8 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.05	–	1.68	0.988	–	0.012	1.09	0.07
C_3	<0.03	–	1.87	0.999	–	0.001	1.40	<0.03
C_5	<0.03	–	1.74	0.998	–	0.002	1.23	<0.03
C_6	0.04	–	1.59	0.996	–	0.004	1.24	0.05
C_8	<0.03	–	1.95	0.999	–	0.001	1.40	<0.03
C_{10}	<0.03	–	1.51	0.997	–	0.003	1.40	<0.03
C_{12}	0.09	0.93	2.61	0.826	0.118	0.056	1.04	0.33
C_{14}	0.24	1.20	3.00	0.426	0.351	0.224	1.07	1.19
C_{16}	0.20	1.05	2.63	0.633	0.311	0.056	0.87	0.60
C_{18}	0.13	0.73	2.19	0.834	0.123	0.042	1.15	0.29

Table 6
Fluorescence lifetime results of various C_n dyes in CTAB solution ([CTAB] = 10 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.09	0.54	2.18	0.955	0.032	0.013	1.09	0.13
C_3	0.10	0.18	2.00	0.937	0.061	0.002	1.28	0.10
C_5	0.16	–	2.03	0.997	–	0.003	1.24	0.16
C_6	0.16	–	1.51	0.995	–	0.005	1.13	0.17
C_8	0.17	–	0.91	0.998	–	0.002	0.84	0.17
C_{10}	0.18	0.35	–	0.992	0.008	–	1.13	0.18
C_{12}	0.16	0.52	–	0.993	0.007	–	0.87	0.16
C_{14}	0.16	0.44	–	0.989	0.011	–	0.80	0.16
C_{16}	0.16	0.58	–	0.996	0.004	–	0.85	0.16
C_{18}	0.16	0.84	–	0.996	0.004	–	0.86	0.16

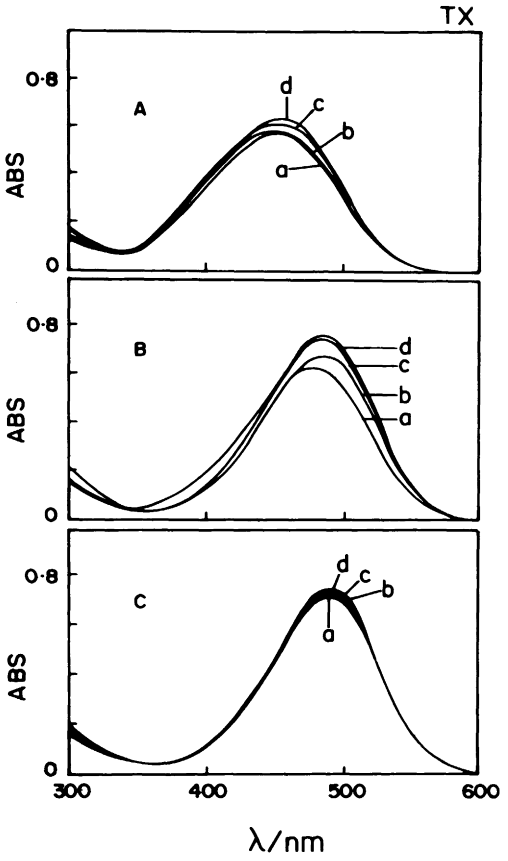

Fig. 5. Absorption spectra for (A) C_3; (B) C_8; and (C) C_{16} dyes in TX solutions for different concentrations: (a) 0.02; (b) 0.06; (c) 0.8; and (d) 11 mM.

solvent. Fluorescent molecules such as the ones studied in this work have the possibility of multiple structures because of the flexibility about the styryl bond, mesomeric structures, and the interaction of the chromophore or solvent (surfactant) with the alkyl chain. The spectroscopic (Table 1) and fluorescence lifetime results (Table 2) in organic solvents are considerably more complex requiring a model of multiple structures in the ground and/or excited states.

Fig. 1 shows the trans, quinoid and cis structures for the dye. It may be noted that the quinoid structure may also be considered as intramolecular charge transfer (ICT) state. Even though the trans and quinoid structures are mesomeric resonance structures, it must be noted that the positive charge is localized on different types of nitrogens in the two isomers; on the pyridine nitrogen in the trans isomer and on the amine nitrogen in the quinoid form. As a result, solvents may interact differently with the two isomers making it possible that either trans or quinoid or both forms to be present in different solvents. It is not possible to predict the role of solvent in stabilizing the trans and quinoid forms by theoretical calculations. Therefore, one has to examine experimental spectroscopic data in a variety of organic solvents to identify multiple structures for the dye in the ground state.

The absorption and emission spectra of the ASP dye are strongly perturbed by the organic solvents. The spectral peak positions, together with absorption coefficients and relative fluorescence intensities, are given in Table 1 for one representative dye, namely C_3. Stokes shift, $(\nu_a - \nu_f)$, is one of the quantitative parameters which is useful to understand the origin of the variation of spectral shift in organic solvents. The Stokes shift

Table 7
Fluorescence lifetime results of various C_n dyes in TX-100 solution ([TX−100] = 0.6 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.06	0.44	1.87	0.927	0.065	0.008	1.12	0.10
C_3	0.03	0.42	1.44	0.936	0.057	0.007	1.10	0.06
C_5	0.19	0.55	1.48	0.666	0.312	0.022	1.11	0.33
C_6	0.20	0.54	1.32	0.617	0.365	0.018	0.82	0.34
C_8	0.22	0.56	–	0.655	0.345	–	0.89	0.34
C_{10}	0.23	0.51	–	0.62	0.38	–	1.03	0.33
C_{12}	0.19	0.46	–	0.581	0.419	–	1.17	0.31
C_{14}	0.20	0.47	–	0.568	0.432	–	1.04	0.31
C_{16}	0.20	0.46	–	0.631	0.369	–	0.88	0.29
C_{18}	0.19	0.46	–	0.577	0.423	–	0.92	0.31

Table 8
Fluorescence lifetime results of various C_n dyes in TX-100 solution ([TX−100] = 11.88 mM)

Dye	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
C_1	0.26	0.65	1.70	0.709	0.198	0.011	1.12	0.33
C_3	0.31	0.74	–	0.781	0.219	–	0.89	0.40
C_5	0.28	0.73	–	0.737	0.263	–	0.89	0.39
C_6	0.26	0.67	–	0.698	0.302	–	0.95	0.38
C_8	0.25	0.66	–	0.663	0.337	–	0.98	0.39
C_{10}	0.33	0.76	–	0.785	0.215	–	1.04	0.42
C_{12}	0.25	0.66	–	0.659	0.341	–	0.95	0.39
C_{14}	0.22	0.63	–	0.615	0.385	–	1.06	0.38
C_{16}	0.22	0.63	–	0.632	0.368	–	0.77	0.37
C_{18}	0.28	0.69	–	0.692	0.308	–	0.87	0.41

Table 9
The absorption (λ_{max}) and fluorescence (λ_{em}) maxima of cis and trans isomers of C_1 dye in various solvents

	Isomer	Water	MeOH	EtOH	$CHCl_3$	Acetone	CH_3CN	Benzene
λ_{max}	Trans	450	479	484	496	476	474	477
	Cis	346, 423	339, 457	336, 462	326, 460	335, 456	330, 440	326, 441
λ_{em}	Trans	581	579	581	560	586	555, 584	552
	Cis	474(sh) 496, 538(sh)	555	555	550 (sharp, sym.)	558	550	548

values are also given in Table 1. Highest value of Stokes shift ($> 4000\ cm^{-1}$) was observed in DMSO, DMF and DMA, and the lowest value ($1636\ cm^{-1}$) in methylene chloride. All the above solvents are polar and hence polarity is not likely to be the reason for the difference in the values. Indeed, a plot of Stokes shift vs. the polarity parameter, Δf (see Table 1 for the equation for Δf relating it to dielectric constant and refractive index) in Fig. 6 shows the absence of correlation of Stokes shift with Δf. (There is a correlation of Stokes shift with Δf among alcohols, as seen in Fig. 6, but we are concerned here with a global consistency.) A linear dependence of Stokes shift and Δf for all solvents validates Lippert–Mataga equation [20] and confirms that the dye has a single structure in the ground and excited states and the slope depends upon the change in dipole moment upon excitation.

Table 10
Fluorescence lifetimes of trans and cis isomers of C_1 dye in various solvents

Solvents	Isomers	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	χ^2	τ_{av} (ns)
Water	Trans	0.04	–	2.16	0.996	–	0.004	1.12	0.04
	Cis	0.06	0.66	2.95	0.961	0.03	0.01	1.04	0.10
Methanol	Trans	0.03	–	2.55	0.999	–	0.001	2.66	0.03
	Cis	0.03	0.45	2.89	0.990	0.008	0.002	0.91	0.04
$CHCl_3$	Trans	0.33	–	1.34	0.20	–	0.80	0.96	1.14
	Cis	0.19	0.72	1.63	0.847	0.081	0.073	1.07	0.33
CH_2Cl_2	Trans	–	0.35	–	–	1.0	–	1.01	0.35
	Cis	0.14	0.37	2.07	0.329	0.665	0.005	1.11	0.30
DMSO	Trans	–	–	–	–	–	–	–	–
	Cis	0.06	0.31	2.57	0.967	0.029	0.004	1.11	0.08
Toluene	Trans	0.07	0.83	–	0.995	0.005	–	1.00	0.07
	Cis	0.08	0.42	3.49	0.962	0.034	0.004	0.88	0.10

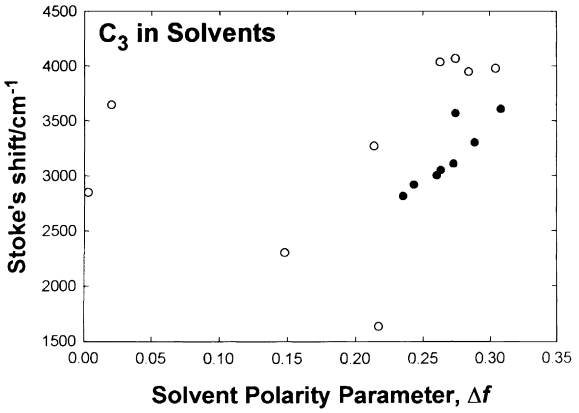

Fig. 6. The plot of Stokes shift versus the solvent polarity parameter (see Table 1). The filled circles are the data for alcoholic solvents (1–8 in Table 1) and open circles are the data for other solvents.

The absence of linear correlation between Stokes shift with Δf (among all solvents) is a clear indication that there is a specific interaction of some solvents with the dye in the ground or excited state or both. Some well-known specific solvent effects on the spectra of dye molecules are hydrogen bonding and charge transfer. If hydrogen bonding is a significant interaction then the spectral shifts are expected to be identical in alcoholic solvents. The variation of Stokes shift from 3600–2800 cm^{-1} among alcohols (methanol to cyclohexanol in Table 1) shows a linear correlation with polarity parameter (Fig. 6). This indicates that polarity effect is more significant than hydrogen bonding effect in alcoholic solvents.

The fluorescence decay of the ASP dyes in most organic solvents is multiexponential. The fluorescence decay in all solvent of moderate viscosity was found to have a major component of short lifetime (τ_1) except in chloroform, methylene chloride, and glycerol. The long lifetime (τ_3) is the major component in chloroform and glycerol but in methylene chloride only middle lifetime component (τ_2) is observed. The most important deviation of the spectroscopic result is observed in chloroform and methylene chloride. The Stokes shift is very low in these two solvents when compared to the solvents of similar polarity and viscosity. Moreover, the fluorescence lifetime of the dye in these two solvents is unusually high. The fluorescence decay and average lifetime in chloroform is comparable to those in glycerol. The fluorescence lifetime of most fluorescent dyes is generally high in glycerol, which is attributed to the high viscosity of glycerol that decreases the collision-induced nonradiative rate in the excited state [20]. However, the viscosity of chloroform is far less than that of glycerol. The experimental results strongly suggest that there is a specific interaction between the ASP dye with chloroform and methylene chloride. The nature of this interaction and the structure of the dye–solvent complex are not clear at present.

The fluorescence of the cis isomer of C_1 in organic solvents was similar to the trans isomer

except for the blue shift of the maximum by 5–30 nm. The fluorescence decay of the cis isomer of C_1 is three exponentials in the six solvents examined (Table 10) including water where the cis and trans isomer of C_1 is soluble. The trans isomer is characterized by a strong component of the short lifetime τ_1. In the case of the cis isomer the middle lifetime τ_2 was also significant. These results suggest that the cis isomer converts to the same excited state as that of the trans isomer giving the τ_1-component in addition to τ_2 which is attributed the excited state of cis isomer.

4.2. Quinoid (or ICT) state

As seen in Fig. 1, the quinoid structure is identical to the charge transfer structure for the ASP dye. It may be noted that a charge transfer state may have a geometry which is comparable with a quinoid structure (as in ASP dye) but a quinoid structure does not have to be a charge transfer state. The charge transfer is responsible for the solvatochromism observed for the compounds investigated. Trans–cis and cis–trans photoisomerization of stilbene-type molecules occur through a common intermediate in excited state, which is sometimes called a "phantom" state [21–28]. In the "phantom" state the dye exists in a quinoid form with a 90° twist of the two aromatic planes on either side of the double bond. This perpendicular configuration (labeled as $Q_\perp$) can exist in other dyes with similar structures such as cyanines and ASP dyes used in this study. The $Q_\perp$ form in ASP dyes may be stabilized by the intramolecular charge transfer (ICT) from pyridinium to dimethyl amino group [29,30]. In more polar solvents the benzenoid form dominates due to hydrogen bonding between solvents and dimethylamino group, whereas the quinoid form is stabilized in nonpolar solvent.

Ikeda et al. [31] have reported that the irradiation of trans isomer of an ASP dye leads to a trans/cis mixture and the short fluorescence lifetime is due to the rapid decay from S_1 to S_0 transition of the trans dye. The lifetime of the "phantom" state ($Q_\perp$) must be shorter than 5 ns since t → c photoisomerization has to be complete within 5 ns as shown by laser flash experiment [32]. Thus, the major component τ_1 could be associated with the trans isomer of the dye and the minor component could be due to the $Q_\perp$ form of the dye.

The spectroscopic and lifetime results indicate that the existence of multiple species of the ASP dye in organic solvent and surfactant solutions. The fact that the spectra were different, though slightly in some solvents where the samples were made from trans or cis isomer, indicates that the interconversion among the multiple species is not very fast. The importance of a stable perpendicular quinoid ($Q_\perp$) configuration in the ground state of asymmetric dyes such as cyanine dyes has been discussed in literature particularly in a nonpolar medium [32,33]. The quinoid form was proposed to be quasi-stable in the ground state [32] but experimental results were supportive of stable quinoid form in excited state only [33]. Based upon the above results, a probable potential energy diagram for the ASP dye involving trans (T), quinoid ($Q_\perp$) and cis (C) forms is represented in Fig. 7.

The quinoid form can be seen in the X-ray crystallographic data of C_1 dye that have been recently reported by Mishra et al. [34]. In crystal, the phenyl ring plane is twisted with respect to the

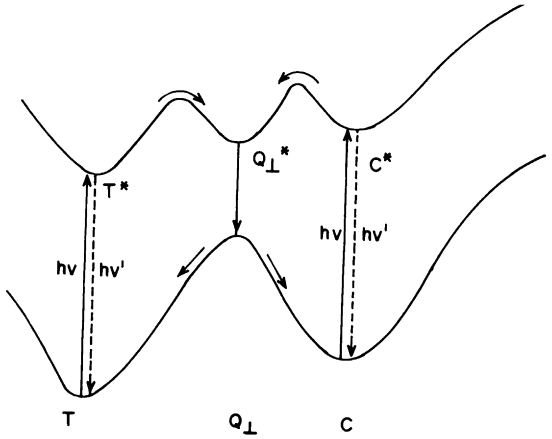

Fig. 7. Potential energy diagram involving the three isomers, trans (T), quinoid ($Q_\perp$) and cis (C), of the aminostyryl pyridinium dye in organic solvents and in surfactant solutions. The quinoid form is a quasi-stable intramolecular charge transfer (ICT) intermediate structure between cis and trans isomers.

pyridine ring plane by 10.47(3)°. In addition, the phenyl ring with the dimethylamino substituent at C_1 (Let C_1–C_6 be the carbon numbers in the phenyl group and C_1 is the carbon attached to the dimethyl amino group.) exhibits bond lengths characteristic of quinoid structure (see Fig. 1b): the two C–C distances, C_2–C_3 and C_5–C_6, are significantly shorter [1.366(3) and 1.375(3) Å] than the other four C–C distances [C_1–C_2, 1.420(3); C_3–C_4, 1.406(3); C_4–C_5, 1.394(3); C_1–C_6, 1.411(3) Å. Other workers have also suggested from the X-ray crystallographic analysis that the trans ↔ quinoid form of cyanine dye exists as resonance hybrid of each other [35,36] in the ground state. In the case of ASP dyes, being positive charge present located at two different types of nitrogens in the molecule in the two resonant forms; some specific solvents can stabilize these two structures to different extents.

In summary, all fluorescence results of trans and cis isomer in organic solvents lead to the conclusion that the short lifetime ($\tau_1 < 0.3$ ns) is attributed to the emission from trans isomer. The middle lifetime ($\tau_2 = 0.4$–0.8 ns) is due to the cis form and the long lifetime ($\tau_3 > 1$ ns) component is attributed to the perpendicular quinoid ($Q_\perp$) or ICT form, respectively.

4.3. Structure of the dye in surfactant solutions

The spectra and fluorescence lifetimes of ASP dyes in organic solvents do not depend upon the length of the alkyl chain in the dye. The effect of the alkyl chain is however observed in aqueous media that promotes aggregation of dye molecules and/or limit the solubility of the dye. Addition of surfactants to the aqueous solution increases solubility of the dye. The surfactant is an amphiphilic molecule and hence the interaction of the ASP dye with different types of surfactants have shown interesting variations with the concentration of the surfactant, particularly premicellar and micellar concentration, and the length of the alkyl chain in the dye.

Our major aim in this study was to investigate the importance of multiple structures for the dye in different solvent environments. The dye dissolved in surfactant solutions is in a new kind of solvent environment depending on the site of solubilization (aqueous side, interfacial region or core region of the micelle). The spectra and fluorescence lifetimes of the dye in surfactant solutions are therefore pertinent for comparison with those of organic solvents. The experimental results for the 10 ASP dyes in three surfactant solutions display considerable complexity. In particular, premicellar surfactant solutions promote aggregate structures for the dye whereas the results in micellar solutions are attributable to the monomer of the dye and thus comparable to those in organic solvents. These are discussed below.

4.4. Micelles as solvents

The absorption spectra (curve d in Figs. 3–5) of the ASP dyes (C_3, C_8 and C_{16}) in SDS, and TX solutions, and (C_8, C_{12}, C_{16}) in CTAB solution above cmc, are similar to those of organic solvents. As in organic solvents, the spectra are independent of the alkyl chain length of the dye. There are no anomalous features in the spectra as observed in premicellar solutions (see below). The dye to micelle ratio is 1 : 100 (or more) and according to the Poisson distribution law, 99% of the dye will be distributed as monomer in micelles [37]. Thus, it is interesting to compare the fluorescence lifetime results for the ASP dyes in the three micelles (Tables 4, 6 and 8) with those of the dye in organic solvents (Table 2).

The fluorescence decay of ASP dyes in CTAB micelle (Table 6) is dominated by the short lifetime component τ_1, independent of the alkyl chain length. The middle (τ_2) and long (τ_3) lifetime components are less than 1% in most cases. Similarly, the fluorescence decays in SDS micelle (Table 4) is dominated by the short lifetime component. The results in SDS and CTAB micelles are similar to that of the dye in methanol except that the value of $\tau_1$is higher in micelles that may be attributed to a higher microviscosity in micelles [18]. τ_2 and τ_3 components are observed in slightly large fractions (3–15%) in some cases (C_1 and C_3 dyes in CTAB and C_{14}, C_{16} and C_{18} dyes in SDS). These are similar to the observations in solvents like dioxane and glycol. It is likely that the

emission may be from those molecules, which are located near the interface.

The fluorescence lifetime results in TX micelle are completely different (Table 8). The fluorescence decay is two exponentials (except C_1 dye) and the amplitudes of the lifetimes (τ_1 and τ_2) are significant. The long lifetime τ_3 is observed only as a minor component in C_1 dye. Remarkably, the fluorescence decay is similar for all dyes (except C_1) as evident from the lifetimes and relative amplitudes and average lifetimes in Table 8. The absorption spectra for the ASP dyes were also similar in TX micelles (curve d in Fig. 5). It appears that TX-100 micellar environment favors the coexistence of cis and trans isomers. Micellar environments are known to affect the interconversion between cis and trans isomers [38,39].

4.5. H-aggregates in premicellar solutions

Premicellar surfactant solutions (surfactant concentration below cmc) may be considered to consist of a distribution of surfactant aggregates, which are not fully formed micelles. Organic dyes may interact differently with surfactants and formation ordered dye aggregates such as J- and H-aggregates that are particularly favorable in some cases such as porphyrins [12]. J- and H-aggregates are unstable in fully formed micelles leading to solubilization the dye only as monomers [12].

The structure and spectroscopic characteristics of J- and H-aggregates have been extensively discussed in literature [40,41]. Briefly, J-aggregate is a side-by-side arrangement of dye molecules such that the transition moments are parallel and collinear. H-aggregate is a face-to-face arrangement of molecules. Theory predicts that the absorption spectrum of the J-aggregate is red shifted and that of the H-aggregates, blue shifted. In addition, the spectrum of the aggregate is narrowed by $N^{1/2}$ where N is the aggregation number [40,42]. Thus, the spectral shift and narrowing of absorption spectrum of the organic dye under conditions, which promote aggregation, are direct spectroscopic evidences for the formation of ordered aggregates.

Figs. 3 and 5 show the absorption spectra of C_3, C_8 and C_{16} dyes in SDS and TX surfactants and Fig. 4 shows the absorption spectra for C_8, C_{12} and C_{16} in CTAB surfactant. Curve 'a' in the spectra is obtained for the surfactant concentration of 0.02 M, which is premicellar for all the surfactants. A blue-shifted absorption band(s) for the C_{16} dye in CTAB and SDS is observed (but not in TX solutions). The absorption spectrum is also narrowed by a factor of 2–3 indicating that the spectroscopic aggregation number is 4–9. It is meaningful to compare other literature reports of H-aggregate of organic dyes based on the observation of blue-shifted narrow spectra [43,44].

We would like to comment in passing that premicellar solutions do promote dye surfactant aggregates of colloidal dimensions (turbidity) in some ASP dyes. The anomalously low intensity of the absorption for C_3 dye in SDS (Fig. 3A, curve b) and C_{12} dye in CTAB (Fig. 4B, curve b) are due to precipitation of the dye.

5. Conclusions

The absorption, fluorescence emission spectra, and fluorescence lifetimes of 10 aminostyryl pyridinium dyes with various lengths of alkyl chains were investigated in organic solvents and in surfactant solutions. The results indicated multiple structures for the dye in most organic solvents and in surfactant solutions. The results are interpreted in terms of the emission from three isomers, trans, cis and quinoid forms of the dye. The relative intensities of the three isomers depend upon the dye–solvent and dye–surfactant interactions. Among surfactant solutions, SDS and CTAB form dye–surfactant complexes in premicellar concentration of the surfactant. The cis isomer is favored in TX-100 solutions.

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