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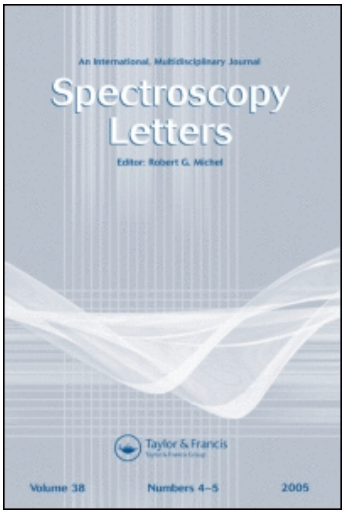

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Excited State Proton Transfer of Carbazole in Aqueous Micelles in the Presence of Urea: Expulsion of the Probe from the Micellar Environment

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EXCITED STATE PROTON TRANSFER OF CARBAZOLE IN AQUEOUS MICELLES IN THE PRESENCE OF UREA : EXPULSION OF THE PROBE FROM THE MICELLAR ENVIRONMENT

Key words : Excited state proton transfer, carbazole, micelles, urea.

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ABSTRACT

Steady state as well as time-resolved decay analysis techniques have been adopted to study the excited state proton transfer (ESPT) reaction of carbazole (CAZL) in three aqueous micellar solutions, namely, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and triton X-100 (TX) in the absence as well as in the presence of urea. For all the micellar systems studied, multiple critical micellar concentrations (CMCs) have been observed. Urea is found to inhibit the micellisation process. Light has been thrown on the mode of

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action of urea. It has also been shown that urea expels the fluorophore molecule from the micellar periphery to the bulk aqueous phase.

INTRODUCTION

Because of the diverse applications of the micellar systems, principally, because of the likeliness of the micelles with proteins, enzymes etc. and thus mimicking the biological systems, attention has been drawn, over the last three decades, to the micellar effects on the nature and the fates of reactions [1-4]. There are two basic intentions for the studies : (i) to see the modifications of the reactions due to the change in the microenvironment from the bulk medium to the micelles around the probe and (ii) to look at different micellar characteristics probing some known reactions. Excited state proton transfer (ESPT) is a very fascinating reaction to the photochemists since this is the simplest chemical reaction with a real movement of some component. Through a series of investigations [5-12] the ESPT of carbazole (CAZL) is now well characterised and can be used to study different aspects of microenvironments like cyclodextrins [8-10], micelles [11, 12] etc.

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Urea, on the other hand, is known to denature biological systems like proteins, lipids etc. A similar type of action of urea on micellar solutions (simpler model systems for the biological environments) is also under investigation in recent years [10, 12-17]. Although, without a loss of generality, urea inhibits micelle formation in the aqueous surfactant solutions, there remains, however, controversy regarding the mode of action [10, 12, 15-20]. While some groups believe that urea 'breaks' the water structure others believe that urea displaces some water molecules from the periphery of the micellar units; the stabilisation of the units, thus, being modified and hence the critical micellar concentrations (CMCs) change.

Carbazole is an interesting fluorophore molecule as during the excited state proton transfer (ESPT) reaction both its neutral as well as the anionic species have strong fluorescences. The ratio of the fluorescence yields of the two emissions, thus, allows one to monitor the progress of the ESPT reaction as well as to study the environment around the probe in some detail [8-12].

In the present paper we report our ESPT study of CAZL in different aqueous micellar systems in the absence and in the presence of urea. We have monitored the neutral to anion emission intensity ratio (N/A) as well as the excited state lifetime of the neutral species of CAZL at a definite pH (= 12) to determine the CMCs in different micellar environments, viz., CTAB, SDS and TX. Our experimental results reveal multiple CMCs for all the three micellar systems. The study also explores the mode of action of urea with the micelles.

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EXPERIMENTAL

Materials :

Carbazole (CAZL) was purified as before [5]. The purity of the compound was checked from the spectroscopic methods as well as TLC where only a single spot could be noticed. CTAB and SDS (both from Aldrich) were recrystallised from water before use. TX (Aldrich) was, however, used without further purification. The micellar solutions were prepared just before the experiments to avoid aging of micelles [21]. Analytical grade NaOH and urea (both from BDH) were used as received.

Measurements :

Shimadzu MPS 2000 absorption spectrophotometer and Spex fluorolog spetrofluorimeter were used for recording the absorption and emission spectra

respectively. The fluorescence decay analysis experiments were performed adopting the time correlated single photon counting (TCSPC) technique [22]. The instrumental set-up is described elsewhere [23].

RESULTS AND DISCUSSION

Estimation of CMCs

The aqueous solution of CAZL (1 x 10^{-5} M), in the absence of external base (NaOH), yields a single but structured fluorescence with maximum at ≈ 360 nm. With the addition of NaOH, a new red-shifted broad emission with maximum at ≈ 420 nm, corresponding to the anion, develops at the cost of the 360 nm neutral emission [5]. Taking the advantage of the dual luminescence of the photoexcited CAZL and its anionic form, it is possible to determine the CMCs of the micellar solutions. For the steady state experiments with the micellar solutions, we have estimated the intensity ratio of the neutral to the anionic emission (N/A) with the variation of the concentration of each of the surfactants at a fixed probe concentration (1 x 10^{-5} M). Figure 1 depicts the nature of variation. The breaks in the plots, as the standard convention, correspond to the CMCs.

The progress of the ESPT reaction in the aqueous micellar solutions is also reflected through the lifetime of the excited neutral species of the fluorophore (τ_{360}). The decay of the anionic species, however, remains practically independent of the change of the environment. This is ascribed to the extreme slow rate for the back protonation of the anion in the excited state as compared to the deprotonation as well as the decay rates of the excited species [5, 6]. τ_{360} has, thus, been monitored and plotted against the surfactant concentrations. Figure 2 depict the nature of such variation. Both of the data sets (figs. 1 and 2) reveal that for all the three aqueous micellar systems there exist more than one CMCs; typically, two for each of CTAB and TX and three for SDS. The CMC values obtained from the

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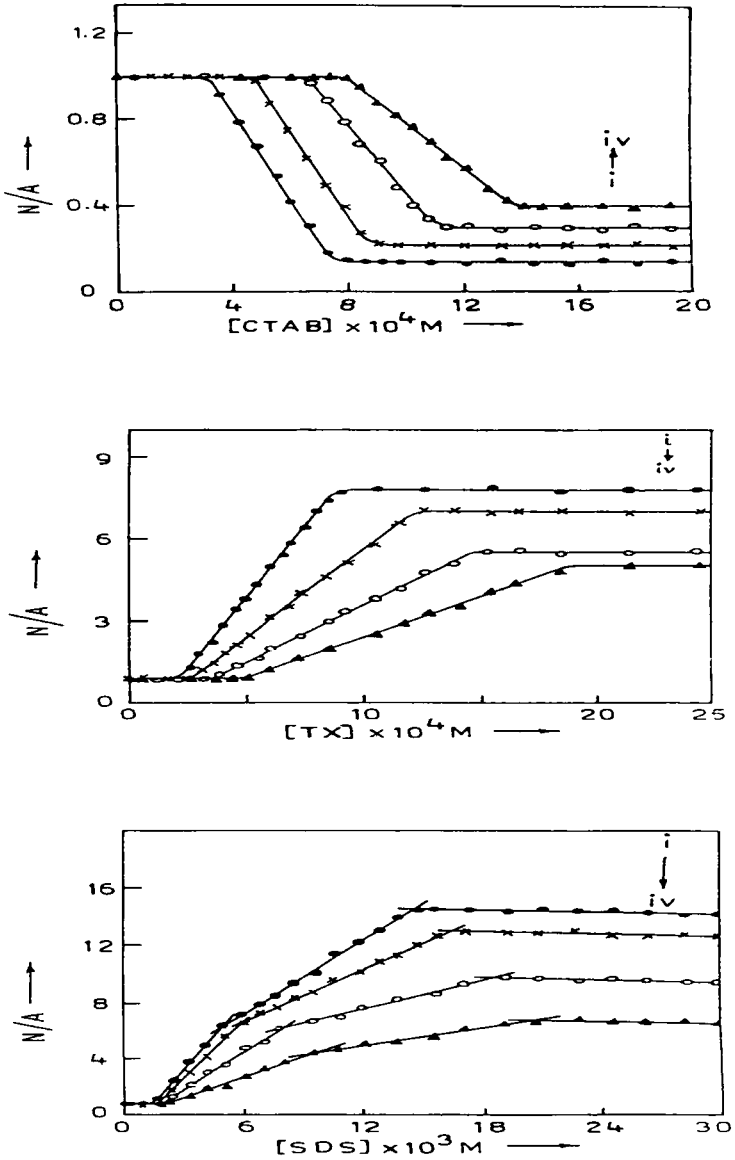

Figure 1 : Plot of N/A against CTAB, TX and SDS concentrations in the presence of urea. i → iv represents 0, 1, 2.5 and 4 molar urea in the solution respectively.

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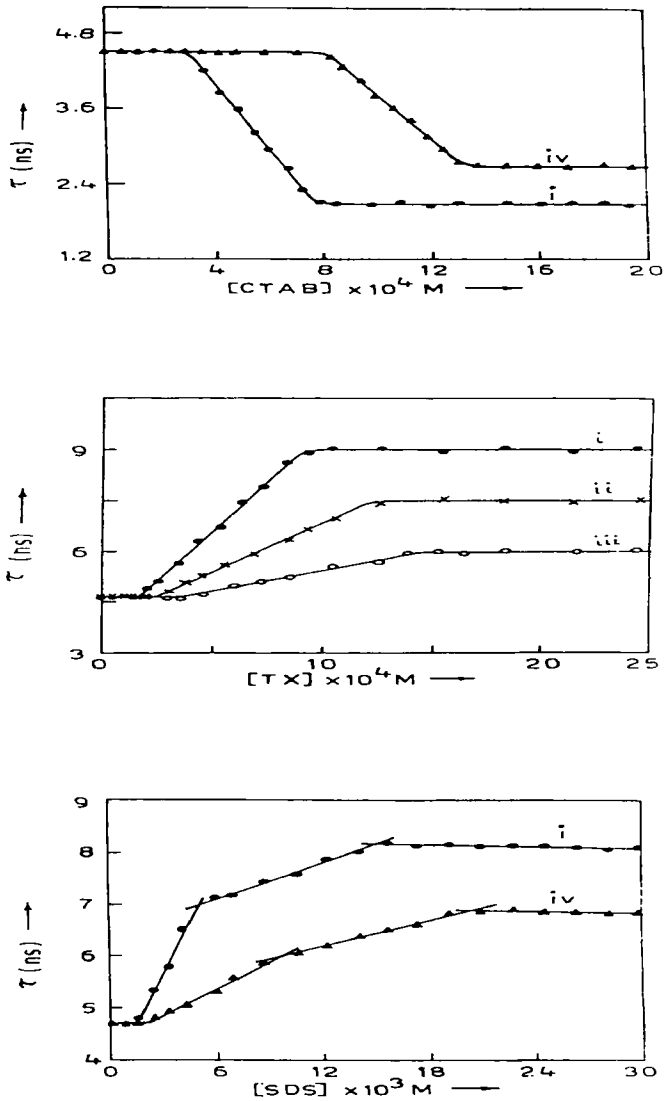

Figure 2 : Plot of τ_{360} against CTAB, TX and SDS concentrations in the presence of urea. i → iv represents 0, 1, 2.5 and 4 molar urea in the solution respectively.

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steady state measurements correspond, extremely well, to the CMCs estimated from the time-resolved study. The CMCs for all the three systems are tabulated in Table I.

Reporting of the multiple CMCs for all the micellar systems studied demands attention. Existing literature report two CMCs only for the SDS system; for the other two, single CMCs are cited [11, 24]. In a recent publication we reported, for the first time, the double CMCs for the CTAB system [12]. Our estimated CMC values [12] for this surfactant system agree, extremely well, to the CMC values reported individually [12, 24, 25], although both were assigned to the CMC_1. Existence of the multiple CMCs for aqueous CTAB and SDS systems has also been reflected from our study of twisted intramolecular charge transfer (TICT) process of p-N, N-dimethylaminobenzonitrile (DMABN) in the said environments [25]. The CMC values obtained through the TICT study (2.5×10^{-4} and 10.0×10^{-4} M for CTAB and 20×10^{-4}, 60×10^{-4} and 150×10^{-4} M for SDS system) in absence of the external alkali are in good agreement with the values determined from the present ESPT study. The small difference in the CMC values obtained through the two methods is believed to be due to the presence of NaOH in the solutions for latter process. Fadnavis and Engberts observed similar multiple breaks when they plotted the specific conductivity against SDS concentration [26]. However, the observation of their experiment was rationalised by the formation of mixed micelles.

To have a discussion on the multiple CMCs of the micelles, let us start from the solution when the surfactant concentration is very low. At this position the N/A or τ_{360} (henceforth to be termed as 'property') are likely not to change dramatically with the addition of surfactants till a minimum concentration of the surfactant, i.e., CMC_1, is attained. Thus, for all the three systems, the flat portions at the beginning of the plots are rationalised. In the earlier reports [11, 24] for the SDS system, one finds that a gradual but rapid change in the properties of the

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TABLE I

Estimated CMCs for aqueous CTAB, TX and SDS Systems in the Presence of Urea.

Surfactant	Urea (M)	CMC x 10^4 (M) estimated through					
		Steady state study			Decay analysis		
		CMC_1	CMC_2	CMC_3	CMC_1	CMC_2	CMC_3
CTAB	0.0	3.0	7.5	a	3.0	7.6	a
	1.0	4.5	8.8	a	b	b	b
	2.5	6.5	11.2	a	b	b	b
	4.0	8.0	13.8	a	8.2	13.7	a
TX	0.0	2.0	9.0	a	1.8	8.9	a
	1.0	2.6	12.0	a	2.5	12.1	a
	2.5	3.6	14.5	a	3.4	14.7	a
	4.0	5.0	18.5	a	b	b	a
SDS	0.0	15	50	147	15	50	150
	1.0	17	60	165	b	b	b
	2.5	19	81	186	b	b	b
	4.0	21	96	206	20	95	204

a : does not exist, b : experiment not performed.

probe starts right from the beginning of the SDS concentration axis. This is very unlikely. Unless micelles are formed (requiring attainment of the first CMC) and the fluorophore does not feel the micellar environment, differing considerably from the bulk aqueous phase, the photoproperties are expected to remain almost invariant (or to change marginally) with the variation of the surfactant concentration. Thus, a gradual and rapid change in the photoproperty of the probe,

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really means that the observer has overlooked and crossed the first CMC and searched for the higher CMCs. To our belief, this is the case with the aqueous SDS system. The second and third CMCs obtained from the present experiment, however, match with the literature values reported, so far, as the first and second CMCs of the system respectively. The present experimental results and the results obtained from the study of TICT of DMABN in micellar media [25] lead us to conclude that the existing literature CMCs of aqueous SDS system correspond to the second and third CMCs and the CMC_1 is considerably less than the second CMC.

Each one of the steady state and time-resolved plots show two plateaus; one at the beginning till the attainment of the first CMC and another at the right end indicating that no further change in the property of the probe occurs with further addition of the surfactants. From the observations, we propose that no further CMCs are expected for the three studied aqueous micellar systems after the final CMCs reported here, viz., CMC_2 for CTAB as well as TX and CMC_3 for SDS.

Interpretation of the multiple CMCs is not, however, obvious at the moment. To our belief, it is a reflection of some phase transformation corresponding to a change in the micellar size and/or shape. This may also indicate the formation of mixed micelles [26]. It is also not clear why does the aqueous SDS system have three CMCs when the other two (CTAB and TX) have two. A study of micellar aggregation number, size and shape at different surfactant concentrations, is likely to resolve these problems.

Interaction of urea with micelles

It is evident from the figures that the addition of urea modifies the CMCs for all the aqueous micellar systems studied. It is important to note that the modification is always to increase the CMCs with the addition of urea indicating that micellisation is restricted in its presence. This corroborates the denaturing

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action of urea in biological systems. However, the basic nature of the variation of the plots (N/A or τ_{360} vs. surfactant concentration) do not change by the presence of urea.

Since there is virtually no change in the photophysical property of the probe before the attainment of CMC_1 even in the presence of urea, for all the micelles, we infer that urea has hardly any influence on the ESPT process below CMC, and it has hardly any effect on the water structure [12, 17-20].

As the surfactant concentration reaches CMC_1 or goes above it, urea affects the N/A or τ_{360} values appreciably. In the presence of urea in the micellar solutions, a change in the relative fluorescence yield is observed at a much higher surfactant concentration as compared to that in its absence (fig. 1). The lifetime of the neutral CAZL (τ_{360}) also starts to deviate much later in its presence (fig.2). These imply that in the presence of urea, the CMCs of the surfactant solutions increase. The CMC values for the aqueous CTAB, TX and SDS systems in absence and in the presence of urea are tabulated in table I. The discrepancies between the values in absence and in the presence of urea are too large to be explained by urea induced change in the microviscosity and micropolarity of the micellar environments [11, 12].

In the absence of urea, the relative fluorescence yield (N/A) of the aqueous CAZL solution in the presence of added NaOH is $\approx$ 1.0 (NaOH concentration = 0.01 M) and the ratio finally drops to $\approx$ 0.15 for CTAB and increases to $\approx$ 8 and $\approx$ 14.5 for TX and SDS systems respectively after the attainment of the final CMCs. It is interesting to note that with the addition of urea to the solution, under similar experimental conditions the final value of the N/A ratio gradually goes up for CTAB system and for a 4M urea solution it is as high as 0.4 (fig. 1a). For the other two micellar systems, this ratio goes down and in the presence of 4M urea the values are 5 and 6.8 respectively (fig. 1).

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Thus, in the presence of urea, even after the final CMC is attained, the ESPT has been disfavored as compared to in its absence. The same is also revealed from the change in the lifetime of neutral CAZL in the three micellar solutions (fig. 2).

We know that CAZL locates itself within the micelles at the peripherial zone resulting in experiencing great influence of the surface charge of the micellar units [8-12]. Thus, the ESPT is favored in cationic (CTAB) and disfavored in anionic (SDS) and to some extent in the non-ionic (TX) micelles [11] and, hence, N/A as well as τ_{360} decreases in the CTAB system compared to the corresponding values in pure aqueous solution. As expected, the corresponding values are increased in the other two micellar systems. An analytical look at the modifications of the 'property (N/A and/or τ_{360}) by the presence of urea in different micellar solutions leads us to propose that urea displaces some of the fluorophores from the micellar environments to the bulk aqueous phase. The possibility of urea induced penetration of the fluorophore into the micellar core is ruled out on the following ground. Since the core is hydrophobic, it is hard for the OH^- to reach the excited CAZL residing there and hence the ESPT is expected to be restricted. This would lead to a biexponential decay of CAZL, with a longer component corresponding to a value of about 8 nanoseconds (τ_{CAZL} depends slightly on the solvent polarity and is $\approx$ 8 ns in alcoholic or even cyclohexane solvents). However, the neutral decays are found to be single exponential with τ values much less than 8 ns (and depends on the external alkali concentration) in all the micellar systems. Thus, carbazole molecules are pushed, not to the micellar core, but to the bulk aqueous phase. In a recent communication, we have established that urea expels the fluorophore CAZL molecule from the cyclodextrin (CD) cavity to the bulk aqueous phase [10]. Based on the report in the aqueous CD environment (rigid and simpler system than micelles) we are confident to report that for the present micellar systems also urea removes some water molecules from the micellar periphery and the destabilisation of the micellar

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aggregates and hence desolvation of the probe molecule at the micellar interface compels it to go to the bulk aqueous environment.

CONCLUSION

The experimental result reveals that urea is not a water structure breaker in the micellar solutions; rather it supports the proposition that some of the solvent molecules at the micellar periphery are displaced by the urea molecules to show the denaturing action of the latter. It also establishes that the probe molecule is expelled from the micellar environment to the bulk aqueous phase.

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