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Interaction of 8-hydroxypyrene-1,3,6-trisulphonate in alkyltrimethylammonium bromide (C_nTAB) micellar medium

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Abstract

Interaction of 1-hydroxy-pyrene-3,6,8-trisulphonate (HPTS) has been investigated in well-characterized, monodispersed, micellar media of cationic surfactants of a homologous series having the general formula C_nTAB and with trisodium citrate, employing absorption and fluorescence spectroscopy. The interaction of HPTS with cationic micelles depends on the hydrophobic chain length of the cationic surfactants. The binding constant of HPTS with C_nTAB micelles decreases with decreasing n. Micelles have strong effect on the interaction of HPTS with trisodium citrate. Fluorescence of HPTS is quenched by citrate ion at the surface of the micelle and the rate of fluorescence quenching decreases with decreasing alkyl chain length of cationic surfactants.

Keywords: HPTS; Micelles; Fluorescence; Quenching

1. Introduction

Due to the importance of micelles as model system mimicking biomembranes in biological processes, attention has been drawn, to the effect of micelles on the nature and rates of reactions [1–7]. Although, the complexity of life systems sometimes keeps us away from obtaining deep insight into the life phenomena because too many factors have to be considered in an *in vivo* system. The properties observed in reconstituted *in vitro* systems, how far is represented in the *in vivo* system is an intriguing question. We always need a simple system with controllable parameters to manipulate and to deduce the fundamental rules that govern the various life phenomena. For that reason an *in vitro* system that mimics the *in vivo* condition always has been a topic of research. Surfactant entrapped water molecules, provide unique microenvironments for interactions and reactions. Water molecules, which are tightly bound to the surfactant head groups of micelles, resemble the hydrophilic pockets of enzyme and have high viscosities, low mobilities, and polarities [8,9]. Proton transfer is fundamental in many natural processes, e.g. transport of a proton through a membrane [10]. The primary step of proton transfer process has been widely studied in many organized assemblies [11–14]. Ground and excited state proton transfer of HPTS [15–21] and other probes [14,22–25] have been studied with great interest in water [17,18], micelle [21–24], reverse micelle [20], and biomolecules [15,16]. Owing to its non-toxic and pH sensitivity HPTS can be used to study *in vivo* system. Gan et al. loaded HPTS via purinergic receptors or hypotonic stress to measure cystosolic pH [26]. There is a sharp fall of pK_a of HPTS from ~7.4 in the ground state to 0.4 in the excited state [17]. In water, HPTS produces a weak emission band at 440 nm corresponding to the protonated form (ROH, Scheme 1) and stronger band at 510 nm corresponding to the deprotonated form (RO^-). Excited state proton transfer (ESPT) from HPTS to water takes place in 150 ps and therefore, the ROH emission shows a decay of 150 ps and the RO^- emission shows a rise of 150 ps and decay of 5500 ps [18,19]. Binding of the anionic probe HPTS with cationic surfactant CTAB is very strong, resulting slow ESPT from HPTS. Roy et al. [27] studied the ESPT from HPTS to acetate in CTAB micellar medium. In this work, we tried to explore the role of hydrophobic chain length of the alkyltrimethylammonium bromide cationic surfactants of a homologous series having the general formula C_nTAB on the interaction of HPTS with trisodium citrate.

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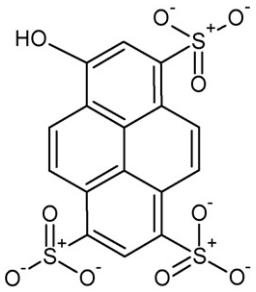


Scheme 1. Structure of the protonated form of HPTS (ROH).

2. Experimental

HPTS was obtained from Fluka and all the cationic surfactants of different chain length of the homologous series C_nTAB namely: cetyltrimethylammonium bromide (CTAB, $C_{16}TAB$), tetradecyltrimethylammonium bromide (TTAB, $C_{14}TAB$) and dodecyltrimethylammonium bromide (DTAB, $C_{12}TAB$) purchased from Aldrich and were used without further purification. Double distilled conductivity water (resistivity > 10) was used throughout the work. The absorption and emission spectra were recorded in a Shimadzu UV-1700 spectrophotometer and a Spex Fluorolog IIA spectrofluorimeter with a slit width of 1.25 mm, respectively. Fluorescence lifetimes were determined from time-resolved intensity decay by the method of time-correlated single-photon counting using a nanosecond diode laser at 370 nm (IBH, nanoLED-07) as light source. The typical response time of this laser system was 1.1 ns. The decays were analyzed using IBH DAS-6 decay analysis software. For all the lifetime measurements the fluorescence decay curves were analyzed by biexponential iterative fitting program provided by IBH. Mean (average) fluorescence lifetime ($\langle\tau\rangle$) for biexponential iterative fitting were calculated from the decay times (τ_1, τ_2) and the preexponential factors (a_1, a_2) using the following relation: $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$.

3. Results and discussion

3.1. Absorbance and fluorescence

The absorption spectra of HPTS in aqueous and in micellar media of CTAB, TTAB and DTAB are given in Fig. 1. Like aqueous environment, absorbance at 405 nm due to the protonated form, ROH (Scheme 1) is strong compared to that at 450 nm due to the deprotonated form, RO^- (Scheme 2). Both in aqueous and in cationic micellar media, with increasing concentration of trisodium citrate the absorbance of RO^- increases and that of ROH decreases. The ratio of absorbance of RO^- to that of ROH has been plotted as a function of trisodium citrate concentration and depicted in Fig. 2. From the plot it can be said that the formation of RO^- is less in micellar media compared to that in aqueous environment. The formation of RO^- in different media follows the order water > DTAB > TTAB > CTAB. Since the formation of RO^- depends on the pH of the media, the pH in different micellar surface will be different. In different media,

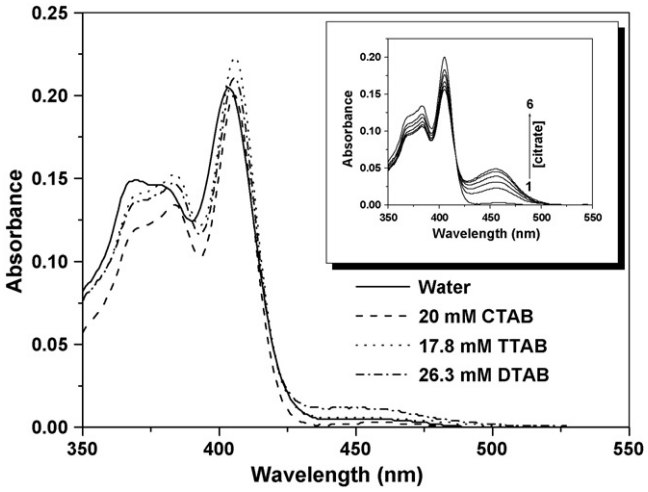
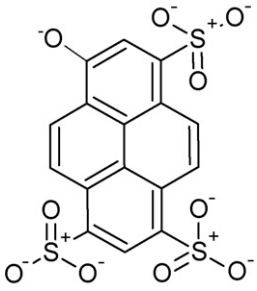


Fig. 1. Absorption spectra of HPTS in different media. Inset: effect of trisodium citrate on the absorbance of HPTS in 20 mM CTAB. [Trisodium citrate]: (1) 0 mM, (2) 1 mM, (3) 2 mM, (4) 3 mM, (5) 4 mM, and (6) 5 mM. [HPTS] = 9.5 μM.



Scheme 2. Structure of the deprotonated form of HPTS (RO^-).

the ratio of formation of RO^- and depletion of ROH increases gradually with citrate concentration and remains constant after a certain concentration of citrate (5 mM) in the solution.

The fluorescence spectra of HPTS in aqueous and in different micellar media have been shown in Fig. 3. In micellar

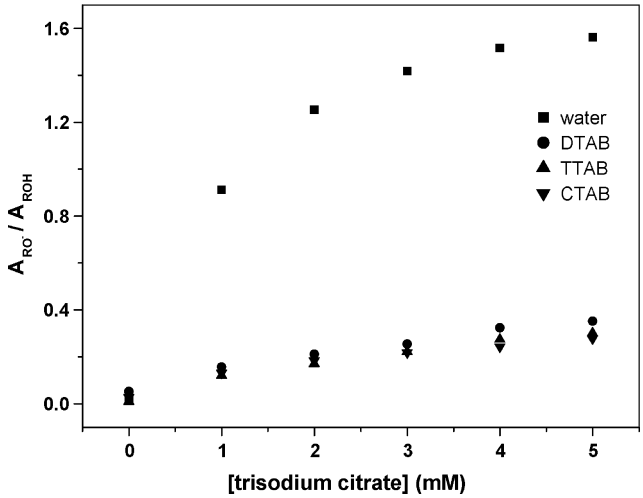


Fig. 2. Plot of relative absorption of RO^- and ROH of HPTS vs. concentration of citrate in different media. [HPTS] = 9.5 μM.

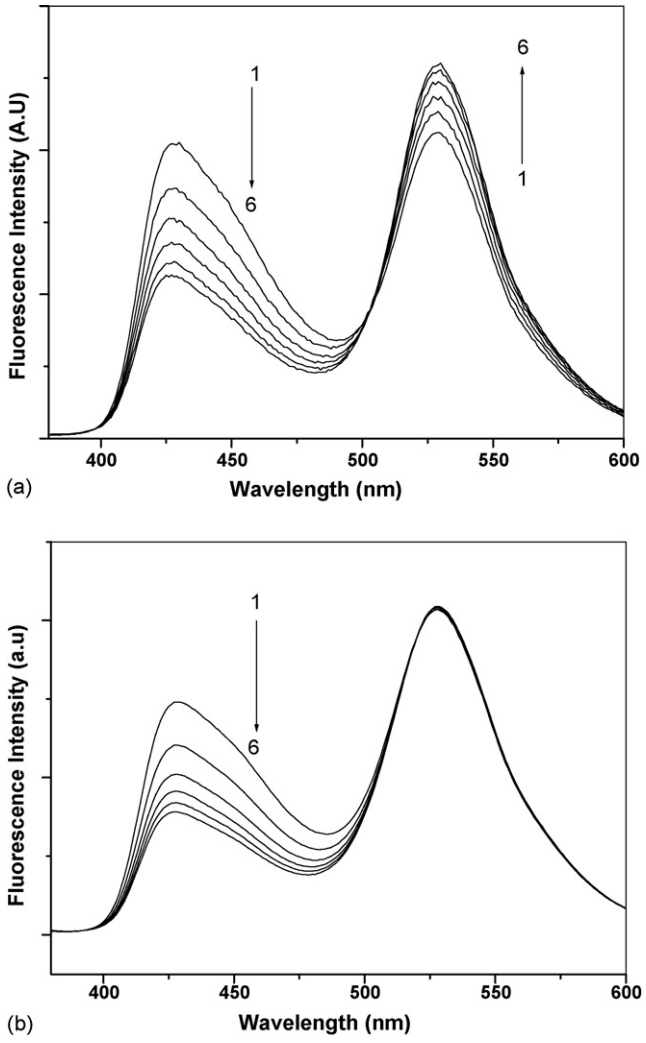


Fig. 3. (a) Fluorescence spectra of HPTS in 20 mM CTAB in presence of trisodium citrate. [Trisodium citrate]: (1) 0 mM, (2) 1 mM, (3) 2 mM, (4) 3 mM, (5) 4 mM, and (6) 5 mM. [HPTS] = 9.5 μM. (b) Fluorescence spectra of HPTS in 26.3 mM DTAB in presence of trisodium citrate. [Trisodium citrate]: (1) 0 mM, (2) 1 mM, (3) 2 mM, (4) 3 mM, (5) 4 mM, and (6) 5 mM. [HPTS] = 9.5 μM.

media the ratio of ROH emission intensity at 427 nm and that of RO^- is higher than that in aqueous media and the intensity ratio of ROH and RO^- in different media follows the order CTAB > TTAB > DTAB > water. This indicates that proton transfer from HPTS is hindered in micellar media compared to bulk aqueous environment and decrement in surfactant chain length favours proton transfer process. In presence of citrate the emission intensity ratio of ROH and RO^- is higher in micellar media compared to aqueous media, which suggests inhibition of proton transfer from HPTS in micellar surface. In micellar media, the fluorescence from the species ROH is quenched by citrate ion whereas the fluorescence from RO^- has been enhanced in CTAB but the fluorescence intensity remains constant in TTAB and DTAB micellar media due to the complete formation of RO^-. This is because, the lower surface area of interface of the micelles of TTAB and DTAB compared to CTAB, the saturation of RO^- in the interface of the micelles of TTAB and DTAB occurs. There exits no equilibrium between ROH and RO^- in these micelles.

3.2. Fluorescence quenching

The quenching of fluorescence of ROH by citrate ion in micellar media of CTAB, TTAB and DTAB has been studied from the fluorescence decay of HPTS at 415 nm (Fig. 4). Biexponential curves were fitted for the decays. Emission at 415 nm is characterized by an initial fast decay that corresponds with the dissociation of the excited molecule. Finally, the curvature declines in a process indicating an approach to a state of quasiequilibrium, where the velocity of dissociation and recombination are equalized. Increasing [trisodium citrate], decay at 415 nm becomes gradually faster with an average lifetime decreasing from 2.377 ns to1.915 ns, 2.231 ns to 1.765 ns and 2.066 ns to 1.726 ns in CTAB, TTAB and DTAB micellar media, respectively, for varying trisodium citrate concentration from 0 mM to 5 mM.

The rate constant of quenching (k_q) of ROH fluorescence by citrate ion has been determined from the relation $1/\tau = 1/\tau_0 + k_q[Q]$, where τ and τ_0 are lifetime of ROH in presence and absence of trisodium citrate, respectively, and $[Q]$ is the local concentration of citrate. Assuming the entire citrate ion present in the interfacial region of micelles, local concentration of citrate was calculated by using those parameters given in Table 1. The linearity of the plot $1/\tau$ versus $[Q]$ indicates one type of quenching occurs (Fig. 5). The quenching rate constants are found to be $2.5 \times 10^8\ M^{-1}\ s^{-1}$, $2.0 \times 10^8\ M^{-1}\ s^{-1}$, $1.4 \times 10^8\ M^{-1}\ s^{-1}$ for CTAB, TTAB and DTAB micellar medium. This is expected since the area of the micellar interface decreases in the same order.

The interface of cationic micelles being positively charged helps the anionic HPTS molecules orient towards the interface by electrostatic attraction. The binding constant (K) of HPTS with the micelles has been determined by using the relation [28]:

$$(F - F_W)^{-1} = (F_m - F_W)^{-1}\left(1 + \frac{1}{K[M]}\right) \quad (1)$$

Rearranging the above equation we get:

$$\frac{F_m - F_W}{F - F_W} = \left(1 + \frac{1}{K[M]}\right) \quad (2)$$

where F, F_W, and F_m represent the fluorescence intensity of HPTS (ROH) in solution, aqueous and maximum concentration of micellar solution, respectively. $[M]$ is the effective

Table 1
Micelle characteristics

Surfactant	No. of carbon atoms in the hydrophobic chain	cmc (mM)	N_{agg}	R (Å)
CTAB	16	0.8	92	35
TTAB	14	3.5	68	28
DTAB	12	15.0	54	24

cmc, aggregation no. (N_{agg}) and micellar radius (R) have been taken from Ref. [29].

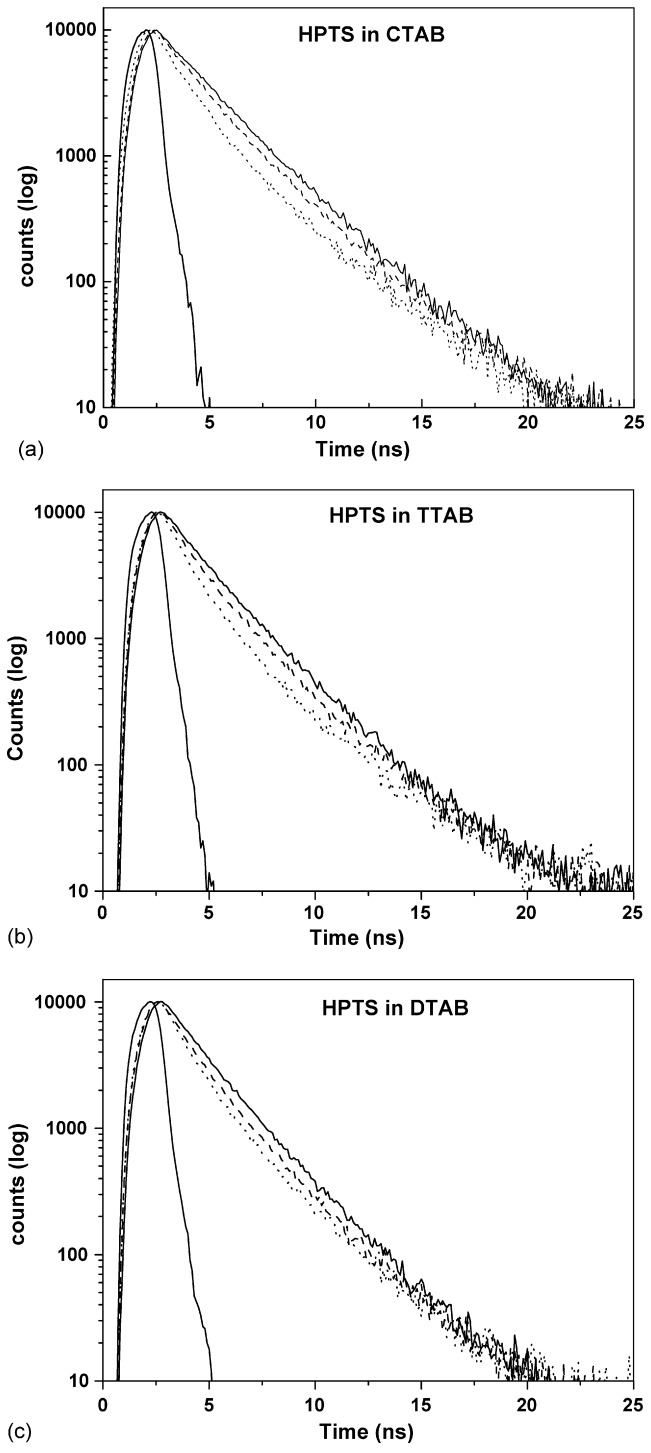


Fig. 4. (a) Fluorescence decays of HPTS in 20 mM CTAB containing 0 mM (—), 2 mM (- - -) and 5 mM (. . .) trisodium citrate; λ_{em} = 415 nm. (b) Fluorescence decays of HPTS in 17.8 mM TTAB containing 0 mM (—), 2 mM (- - -) and 5 mM (. . .) trisodium citrate; λ_{em} = 415 nm. (c) Fluorescence decays of HPTS in 26.3 mM DTAB containing 0 mM (—), 2 mM (- - -) and 5 mM (. . .) trisodium citrate; λ_{em} = 415 nm.

micellar concentration. K values were determined from the slope of the plot $(F_m - F_W)/(F - F_W)$ versus $[M]^{-1}$ and the values were 2.62×10^5 dm^3 mol^{-1}, 1.36×10^5 dm^3 mol^{-1}, 1.18×10^5 dm^3 mol^{-1} for CTAB, TTAB and DTAB micellar

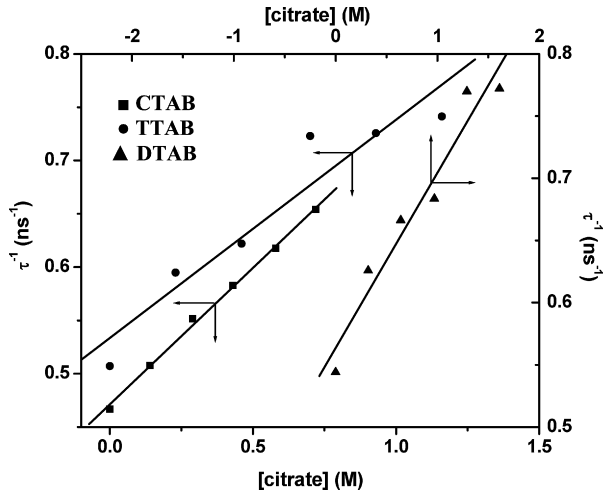


Fig. 5. Plot of inverse of lifetime of ROH decay vs. local concentration of trisodium citrate at C_nTAB micellar interface.

media, respectively. The binding of HPTS with micellar surface causes the slow release of proton from the probe.

The quenching rate constants in micellar media follow the order of the hydrophobic chain length of the surfactants and binding constant of the probe with the micelles. Quenching of fluorescence of HPTS occurs through proton transfer whose rate is different in different micellar media due to difference in binding strength of HPTS with micelles. Hence one can say that the hydrophobic chain length of the cationic surfactants plays an important role in the quenching processes in micellar media.

4. Conclusions

This work shows that the microenvironment of HPTS in cationic micelles is different from that in bulk water. Fluorescence of HPTS is quenched by trisodium citrate in cationic micellar media and the quenching rate constant decreases with increase in hydrophobic chain length of the surfactants. The variation of quenching rate constant in different micellar media may be ascribed to the variation of the binding of the probe with micellar interface. The binding of the probe with micellar interface becomes strong with increase in surfactant chain length.

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