196. Effect of Self-Assembly of Amphiphilic Redox-Chromophores on Photoionization Processes

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Summary

A surfact derivative of phenothiazine was synthesized which is capable of micelle formation in aqueous solution. Concomitantly with micellization, strong changes in the photochemical behaviour occur. In particular, monophotonic photoionization is only observed above the critical micelle concentration (CMC.). Cooperative effects associated with self-assembly of this amphiphilic redox chromophore leading to local electrostatic barriers are evoked to explain these effects.

Introduction. – The study of photoinduced electron transfer reactions in organized molecular assemblies is a fascinating domain of modern research which due to its importance for solar energy conversion currently receives widespread attention [1]. It has been demonstrated unambiguously [2] that the microheterogeneous character of micellar systems, in particular the presence of local electrostatic fields, is ideally suited to achieve kinetic control of the redox events. Particularly intriguing behaviour is displayed by functional surfactants [3] which exhibit cooperative effects assisting light-induced charge separation. Micellar effects on photo-redox reactions become readily apparent [4] when investigating photoionization processes, *i.e.*,

$$S^- \xrightarrow{h\nu} S^+ + e^-_{aq}$$

where S is a sensitizer incorporated into the micelle and e^-_{aq} stands for the hydrated electron. In the present paper an amphiphilic redox chromophore, *i.e.* sodium 12-(10′-phenothiazinyl)dodecyl-1-sulfonate (PTHDS), is used to illustrate striking changes in the mechanism of photoionization as well as the fate of the reaction products associated with the self-assembly of this surfactant.

Results. – *Micelle-forming properties of PTHDS.* The results obtained from tension measurements *vs.* concentration of monomer are presented in *Figure 1*. The breakpoint allows for ready evaluation of the critical micelle concentration (CMC.) as 5×10^{-4} M. It should also be noted from *Figure 1* that the surface tension of the surfactant solutions continues to decrease at concentration above the CMC. This

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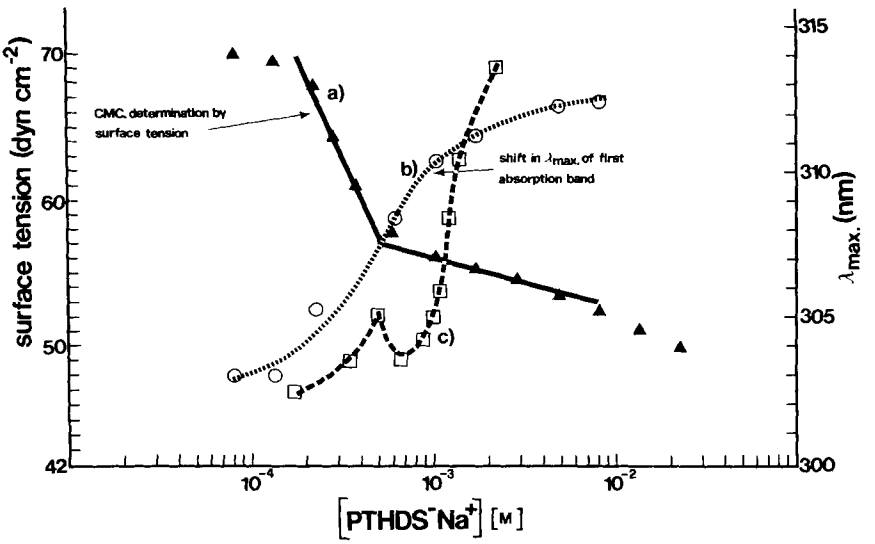

Fig. 1. *Physical properties of 12-(10'-phenothiazinyl)dodecyl-1-sulfonate surfactant plotted against the logarithm of PTHDS concentration:* a) *surface tension,* b) *optical absorption,* c) *light scattering*

implies an increasing degree of aggregation with increasing surfactant concentration.

From the slope of the surface tension *vs.* concentration plot below the CMC. value, the area required by one surfactant head group at the air/water interface is readily calculated as $S = 143$ Å^2/molecule from the *Gibbs* equation. This value implies a rather large area per molecule compared with 51 Å^2/molecule for sodium tetradecyl sulfate, for example. This may, of course, be attributable to the large size of the chromophore inhibiting any closer packing of the hydrophilic head groups.

Curve *b* in *Figure 1* shows a plot of the shift in λ_{max} of the first long wavelength absorption band of the phenothiazinyl chromophore on variation of the monomer concentration. This demonstrates that on micelle formation the chromophore is being incorporated into the interior of the aggregate. The observed red shift with increasing concentration of the monomer is consistent with an electronic transition of 'n-Π^*' character probing a less polar environment. This shift is consistent with that observed for 10-methylphenothiazine in solvents of varying polarity.

The variation of the scattered light intensity at $\theta = 6.7°$ with concentration is shown in curve *c* of *Figure 1*. Again a break point is observed at 5×10^{-4} M [5]. Treating the system as a simple two-component system and applying the *Raleigh-Debye* equation as follows:

$$\frac{K(c-c^*)}{R_\theta - R_\theta^*} = \frac{1}{\nu M_s} + 2B(c-c^*)$$

where c^* is the CMC., R_θ^* is the *Raleigh* factor at the CMC., ν is the aggregation number and M_s is the molecular weight of the surfactant monomer. A plot of $(c-c^*)$ *vs.*

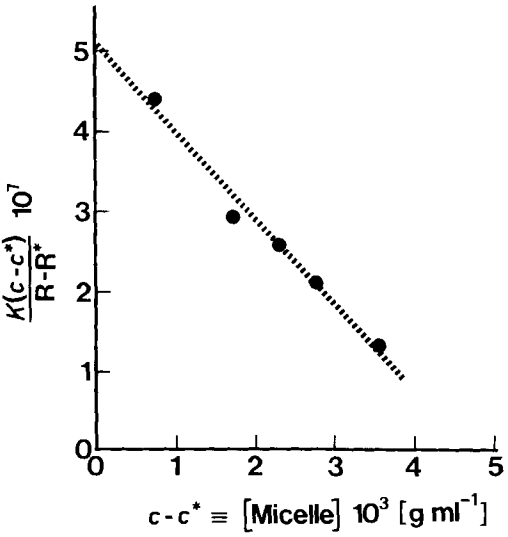

Fig. 2. Zimm *plot of the light scattering data treated by the theory of charge micelles for PTHDS*

$$\frac{K(c-c^*)}{R_\theta - R_\theta^*}$$

gives the *Zimm* plot [6] at the limit of zero angle *(Fig. 2)*. At the limit of $(c-c^*)\rightarrow 0$, the mean micellar weight is determined as 1.98×10^6 a.m.u. The aggregation number ν is then calculated as 4.2×10^3. Such an aggregation number is not compatible with a spherical micellar shape but rather indicates the presence of rod-like structures. The rod-like model is typically consistent with data on large aggregates where an increase in surface-to-volume ratio is often observed [7].

Photophysics. In dilute aqueous solution at 25°, the absorption spectrum of PTHDS is very similar to other phenothiazine chromophores *(Fig. 3)* with a broad absorption band at about 305 nm. In alcoholic solvents of decreasing polarity, the band undergoes a small red-shift suggestive of 'n-Π^*' character in the transitions. Low temperature data and data from *Mantsch et al.* [8] suggests this band to be composed of three closely situated electronic transitions. The existence of three states also explains the apparent large red-shift in the fluorescence spectrum *(Fig. 3)* relative to the absorption spectrum.

On optical excitation under dilute conditions PTHDS exhibits an emission for which the spectrum is displayed in *Figure 3*. The emission maximum is located at 455 nm corresponding to an energy of 2.72 eV. It is concluded on the basis of lifetimes and lack of any appreciable O_2 quenching effect that the emission is originating from the singlet manifold. Furthermore, a comparison with 10-methylphenothiazine corroborates this conclusion since it has a fluorescence emission at 450 nm as distinct from its phosphorescence emission at 490 nm. In ethanol at 77 K, a phosphorescence emission is also observed for PTHDS. The relative area of phosphorescence to fluorescence emission was 698:1.

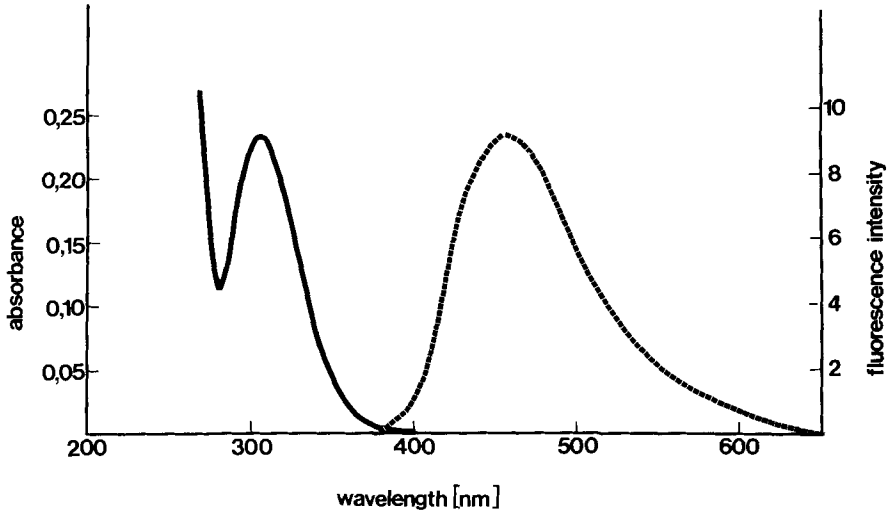

Fig. 3. *Absorption and emission spectra of PTHDS under dilute aqueous conditions: 10 mm P/L. 5×10^{-5}* M

Under dilute conditions the fluorescence quantum yields is 0.004 ± 0.002 at 25°. Fluorescence is not the primary energy loss channel. From the low-temperature studies and from the pulsed experiments, intersystem crossing appears to be very efficient with a quantum yield of nearly unity.

Upon increasing the analytical concentration of PTHDS to above CMC. and monitoring the fluorescence by front-face techniques, the fluorescence profile is neither drastically altered nor does the yield change within the limits of the experiment.

The fluorescent lifetime (τ_F) of PTHDS in homogeneous solution is $\sim1.6\pm0.02$ ns, nearly the same as for 10-methylphenothiazine. The same value is obtained at higher concentrations, greater than the CMC. If the nonradiative decay of the singlet state is principally by intersystem crossing to the triplet state as suggested, then the rate for $k_{isc}=6.0\times10^8\ s^{-1}$. This is consistent with the observation of rapid population of the triplet manifold in a period shorter than the 15 ns laser pulse.

Thus the photophysics of the lowest emitting singlet state are not perturbed upon micelle formation. This is in agreement with observations on phenothiazinyl derivatives incorporated into micelles [3a] or phospholipid vesicles containing phenothiazine [9].

Upon optical excitation by a laser pulse of low intensity of a dilute aqueous solution of PTHDS the transient spectrum shown in *Figure 4(a)* is generated. From quenching studies with O_2 or biacetyl and by comparison with T-T data from other phenothiazine derivatives, it is readily identified as the triplet-triplet absorption spectrum. At concentrations well below the CMC., the triplet state relaxes by typical decay channels (impurity-quenching) back to the ground state. At 25° this process is first-order with a rate $k=2.86\times10^4\ s^{-1}$.

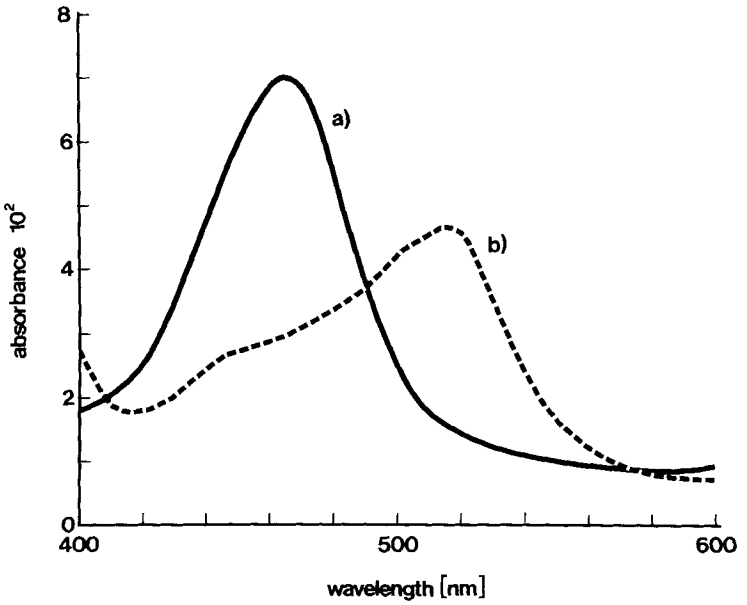

Fig. 4. a) *Transient spectra of PTHDS triplet generated by laser excitation at 353 nm in aqueous* 5×10^{-5} M *solution,* b) *Transient spectra of PTHDS cation generated by laser irradiation of* 2×10^{-3} M *solution of PTHDS*

In order to quantitatively assess the photophysical changes upon micellization, it is necessary to determine the parameters concerning the triplet state.

The triplet extinction coefficient ε_{465} (PTHDS) was determined by energy transfer, by the method established by *Land* [10]. The acceptor was naphthalene which has a lowest triplet state of 2.64 eV. The experiment was carried out in ethanol solution since the statistics of probe distribution and monomer aggregation complicate the analysis of energy transfer in micellar systems. Using naphthalene concentrations to ensure quantitative conversion of $(PTHDS)^T$ to naphthalene triplets, one obtains

$$\varepsilon_{465}\,(PTHDS)^T = (4.87 \pm 0.01)\times 10^4\,M^{-1}\,cm^{-1}$$

The spectral characteristics of the $(PTHDS)^T$ spectrum in ethanol and aqueous solution revealed no change in shape or position of the maxima. This justifies the validity of using $\varepsilon_{465}\,(PTHDS)^T$ calculated in ethanol for the aqueous micellar system. Furthermore, if the Φ_{isc} is assumed to be unity, careful actinometry of the laser-pulsed experiment using a well-defined volume of excitation, gives a value in water of

$$\varepsilon_{465}\,(PTHDS)^T = (4.7 \pm 0.1)\times 10^4\,M^{-1}\,cm^{-1}$$

Actinometry using the pyrene T-T absorption as a standard yielded a Φ_{isc} for $(PTHDS)^T$ in ethanol of

$$\Phi_{isc} = 0.98 \pm 0.05$$

Upon increasing the concentration of PTHDS to one where micelle formation takes place, new features become apparent. The transient absorption spectrum immediately after the laser pulse shows a more complex spectrum, composed of both the $(PTHDS)^T$ spectrum and the $PTHDS^+$ cation radical whose absorption spectrum *(Fig. 4(b))* is recognized from the literature data on other phenothiazinyl derivatives [3a] [4a]. The kinetics of the observed transient decays are also now more complex comprising multi-ordered kinetics.

Some of this complexity can be reduced by looking at a two-dimensional view in wavelength and time and by assuming the validity of *Beer*'s Law for both the cation and the triplet state. For this the extinction coefficient of PTHDS cation was determined in a manner described previously [3a]. This involves a method of quantitative oxidation of PTHDS to $PTHDS^+$ cation by ferricyanide initiated by addition of $CuSO_4$ to the solution and a light-induced electron transfer step. From the slope of the cation decay monitored at 515 nm one obtains

$$\varepsilon_{515}(PTHDS^+) = (6150 \pm 0.04) \times 10^3\,M^{-1}\,cm^{-1}$$

With the knowledge of these parameters and the spectral features for both species,

$$\varepsilon_{465}(PTHDS^+) = 3.320 \times 10^3\,M^{-1}\,cm^{-1}$$

$$\varepsilon_{515}((PTHDS)^T) = 1.322 \times 10^4\,M^{-1}\,cm^{-1}$$

analysis of the data for its two components can be resolved given that the optical density is equal to

$$O.D. = \log \frac{I_0}{I} = (\varepsilon_\lambda^T C^T + \varepsilon_\lambda^+ C^+)$$

The contribution from the solvated electrons at times greater than 5 μs was neglected due to the fast bimolecular decay probably to produce hydrogen [11]. At shorter times, the electron contribution was allowed for, using a modified term for the cation optical density which incorporated a time-dependent electron optical density term based on the above bimolecular process.

Results in *Tables 1* and *2* are obtained after processing data for contributions by triplet and cation from the observed signal at low laser intensity.

From *Table 1*, the triplet lifetime is seen to increase strongly upon increasing the concentration of the monomer, especially above the CMC. value. This significant increase in lifetime is attributable to the increased viscosity of the micelle medium, impeding the quenching of triplets by impurities and ions. The lifetime is then governed by the slow exit of $(PTHDS)^T$ from the micelle [12]. This is seen in the primarily first-order decay of the triplet at high concentrations.

Upon increasing the laser intensity, the triplet decay takes on a new form with the appearance of a short-lived component superimposed on the long-lived decay. When the excitation pulse intensity was varied in the range of 5–100 mJ, the slow decay process was found to be independent of the intensity and the amount of triplet 2 μs after the laser pulse was also invariant once saturation had been

Table 1. *Lifetimes and yields of PTHDS triplet in aqueous solutions of differing [PTHDS]*

[PTHDS]M	τ (μs)[a]	$[(PTHDS)^T]_M$[b]	Φ_{isc}[c]
2.55×10^{-5}	68	2.41×10^{-7}	1.0
6.37×10^{-5}	70	6.31×10^{-7}	1.0
1.10×10^{-4}	82	7.43×10^{-7}	0.78
2.22×10^{-4}	88	8.84×10^{-7}	0.40
5.00×10^{-4}	322	1.03×10^{-6}	0.15
9.10×10^{-4}	448	1.18×10^{-6}	0.093
1.15×10^{-3}	535	1.07×10^{-6}	0.066
2.39×10^{-3}	686	1.98×10^{-6}	0.058

[a]) Lifetimes determined for long-lived component at low laser intensity. [b]) Value determined by extrapolating back to 'zero time' for the long-lived triplet decay and same laser intensity. [c]) Triplet quantum yield assumed as unity at this concentration as explained in text.

achieved. However, the amount of triplet produced, having a fast non-exponential decay, is dependent in a linear relationship on the laser intensity. This observed behaviour strongly suggests that the initial fast decay is due to a fast bimolecular T-T annihilation reaction. In dilute aqueous solutions of 10^{-3} M ethanol solution, this triplet quenching pathway was not observed, infering no ground state quenching mechanism.

An additional feature observed upon micellization is an increase in the relative yield of cation production. Again from *Table 2*, it can be seen that at low concentration, the amount of cation produced is essentially nil and that triplet production is unity. Above the CMC. value the cation production becomes comparable to the triplet production. This can be clearly seen in the plot of Φ_T/Φ_{CAT} with PTHDS monomer concentration in *Figure 5*. This relative enhancement in the cation production has been observed with other systems in which a hydrophobic dye molecule has been incorporated into an aqueous micelle of negative potential [13]. Similarly to these systems, the cation product of photoionization was found to increase nearly linearly with laser intensity, indicative of a monophotonic process. Under dilute conditions, this process was biphotonic in nature *(Fig. 6)*.

This effect is readily rationalized in a shift of the standard redox of the couple $(PTHDS^+/(PTHDS)_0)$ by a few hundred millivolts negative to the micelle potential

Table 2. *Lifetimes and yields of PTHDS cation in aqueous solution of differing PTHDS monomer concentration*

[PTHDS]M	$\tau_{1/2}$	$[PTHDS^+]_{t=0}$M[a])	$[PTHDS^+]_{t=50\,\mu s}$[b])	Φ_{CAT}[c])
2.55×10^{-5}	0.8 ms	2.0×10^{-10}		8×10^{-4}
6.37×10^{-5}		2.1×10^{-10}	6.76×10^{-7}	3×10^{-4}
1.10×10^{-4}	900 ms	3.62×10^{-8}		0.048
2.20×10^{-4}	5×10^2 s	3.77×10^{-7}	1.58×10^{-6}	0.17
5.00×10^{-4}		2.30×10^{-6}	2.30×10^{-6}	0.33
9.10×10^{-4}	$1.19\times10^{+5}$ s	4.31×10^{-6}		0.34
1.15×10^{-4}		4.01×10^{-6}		0.25
2.385×10^{-3}	$1.80\times10^{+5}$ s	3.34×10^{-6}	2.26×10^{-6}	0.1

[a]) Values determined a zero time and normalized to the same laser energy. [b]) Cation concentration at 50 μs after laser pulse. [c]) Determined from relative yields of triplet and cationic species.

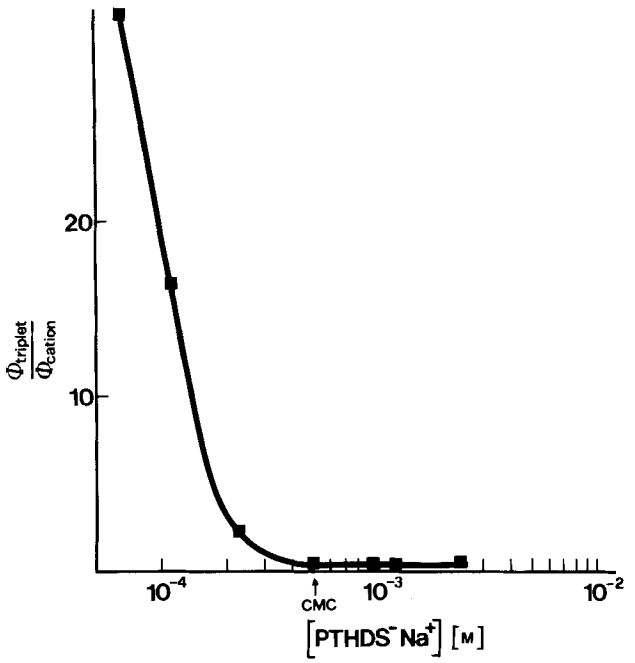

Fig. 5. *Plot of Φ_T/Φ_{CAT} ratio for PTHDS* vs. *the logarithm PTHDS analytical concentration*

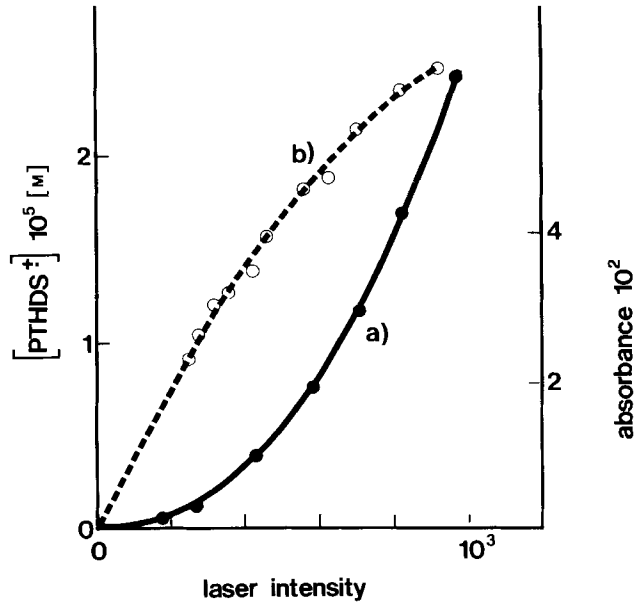

Fig. 6. *Variation of cation yield with laser intensity:* a) *PTHDS concentration less than the CMC.*, i.e., 5×10^{-5} M, b) *PTHDS concentration greater than the CMC.*, i.e., 2×10^{-3} M

[13]. Under conditions where micellar aggregates prevail, the excited state produced by absorption of photons of 3.5 eV energy is sufficient to initiate electron tunneling to the unoccupied levels in the aq/e^+_{aq} system. In the monomer case, rapid population of the triplet level is observed, with photoionization occuring upon subsequent absorption of a second photon of 3.5 eV.

The net effect of micelle formation is then to enhance the cation yield with a subsequent decrease in the yield of triplets observed. Such a correlation is suggestive of a common intermediate state. Since the second excited triplet state is energetically inaccessible in a one photon absorption process, the common intermediate must be in the singlet manifold. Furthermore, it is unlikely to be the lowest emitting singlet state, since the fluorescence lifetime was shown to be invarient to micelle formation effects.

An additional feature is illustrated by the oscilloscope traces in *Figure 7*. Under dilute non-aggregating conditions a slow redox process takes place, since the cation can be seen to grow in with time. On this time-scale the triplet is the only excited species remaining. It must indicate a process involving electron transfer from the triplet state to electron traps in the aqueous bulk. As the monomer concentration increases, the cation grow-in is instantaneous with the laser pulse.

The fate of the cation produced is also worth considering. As has been observed previously, the stability of the cation is greatly enhanced in the micellar environment [3a] [13]. This system demonstrates this clearly by considering the variation in half-lifetime of the cation with concentration. The increase in lifetime above the CMC. value exemplifies the stabilizing features of the micelle. It has already been reported that the hydrated electrons produced by photoionization cannot reenter a negatively charged micelle and recombine with parent cations. Their most likely fate is H_2 production *via* a bimolecular reaction:

$$e^-_{aq} + e^-_{aq} \rightarrow 2OH^- + H_2$$

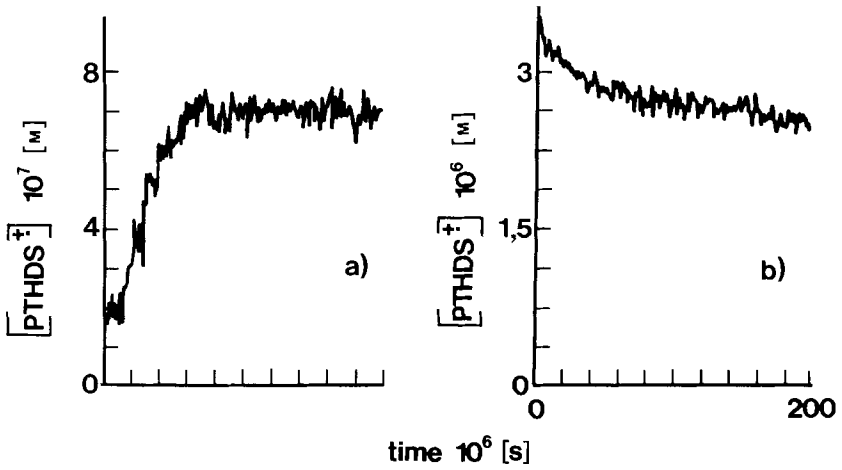

Fig. 7. *The concentration dependence of PTHDS$^+$ cation radical production with time at smaller* (a: 5×10^{-5} M) *and greater* (b: 2.4×10^{-3} M) *concentrations than CMC.*

The e^-_{aq} decay process is experimentally observed.

The loss of $PTHDS^+$ cation then must be controlled by the rate of exit of $PTHDS^+$ cation to the surface of the micelle as has been observed for cations in other amphiphilic environments. Even at pH 10, the micellar effect is strong enough to prevent degradation by hydroxide ions.

At sufficiently high laser intensities and under micelle-forming conditions, the decay of the cation has an initial fast decay with a lifetime of about 2 μs. Although the dependence of the cation yield at $t=0$ upon laser intensity is monophotonic, the initial fast decay always achieves a plateau value of about 1×10^{-5} M, and the PTHDS monomer concentration does not significantly alter this value. It is proposed that each micelle can support only a certain number of cation units before the forces holding the micelle together are negated by the repulsive forces between charged cations. On the basis of this assumption, it would seem that the maximum number of cations per micelle is 22 in a system containing a micelle concentration of 4.4×10^{-7} M.

So though the PTHDS micelle is capable of storing cations for long periods of time, at neutral pH, the packing density of the cations was not particularly high. A nearest neighbor distance for the cations of 119 Å in a rod is a lower limit, since any other shape will have a smaller surface-to-volume ratio enabling cations to be even less densely packed. The absence of any spectral features due to the cation dimer further confirms this [14], though a transient spectrum immediately at the end of the laser pulse does show a slight enhancement at 460 nm where the cation dimer is expected to absorb.

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Experimental Part

Materials. – *Sodium 12-(10′-phenothiazinyl)dodecyl-1-sulfonate.* A solution of 4.6 g (3.65×10^{-2} mol) of Na_2SO_3 in 31 ml of water is added drop-wise within 20 min to a solution of 11 g (2.5×10^{-2} mol) of crude 12-(10′-phenothiazinyl)dodecyl-1-bromide in 92 ml of ethanol and 34 ml of water. The resulting suspension is kept at its b.p. for 10 h. Another 2.3 g of Na_2SO_3 were added after 6 and 8 h, respectively.

The solvents were evaporated *i.v.* The residue is dissolved in hot ethanol. The crude product crystallizes upon cooling. It is filtered off and transferred to a *Soxhlet* extractor for the removal of remaining substrate (solvent: hexane). Recrystallization of the dried product from water gave 2.1 g (18%) of the sulfonate. The product has been characterized by IR., FD., mass spectrometry and elemental analysis.

12-(10′-Phenothiazinyl)dodecyl-1-bromide. A solution of 20 g (0.1 mol) phenothiazine in 40 ml dry tetrahydrofurane is added within 10 min to a suspension of 4.8 g NaH in 60 ml of the same solvent. The orange-colored solution is stirred for 1 h at 40°, then cooled to RT. and added slowly (1 h) to a solution of 70 g (0.21 mol) of 1,12-dibromododecane in 1 l of dry tetrahydrofurane. The red-colored solution is stirred for another hour at RT., for 5 h at 50° and for 12 h again at RT. The resulting suspension is filtered and the solution evaporated *i.v.* The residue containing the product is chromatographed on 3 kg of silica gel (hexane) in order to separate the excess of 1,12-dibromododecane. The product containing silica gel is dried (yield 24.4 g (55%)) and used directly for the synthesis of the sulfonate.

Pyrene and naphthalene (Eastman-Kodak) were purified by chromatography. The micelle solutions were made-up in de-ionized water that had been distilled from alkaline permanganate and sub-

sequently distilled twice from a quartz still. All other compounds employed were analytical grade and used as supplied. The solutions were degassed either by freeze-pump-thaw cycles or by bubbling with high-grade argon for 20 min prior to laser and fluorescence studies.

Apparatus. Steady-state emission experiments were carried out with a *Perkin-Elmer* MPF-44A spectrofluorimeter which is equipped with a corrected spectra unit. The instrument displays true fluorescence spectra, the measured quantity being photon flux per unit wavelength interval. The fluorescence quantum yields were obtained by comparison of optically dilute samples (optical density <0.02) with a standard acidified quinine sulfate solution. All low temperature experiments were studied in an alcohol glass at 77 K. The instrument was suitably modified with *Hitachi M.P.F.* phosphorescence accessories.

Ground-state absorption spectra were measured on a *Varian-Cary* 219 recording spectrophotometer.

Time-correlated experiments were performed with a neodynium or ruby solid-state laser supplied by *J.K. Lasers*. The laser systems (*J.K.*-2000 series) were frequency-doubled or tripled in order to obtain a pulse of suitable wavelength. The laser emission intensity could be readily controlled up to 100 mJ/pulse and checked by using a 'black glass' calorimeter made by *Laser Instrumentations*. Single Q-switched pulses of 15 ns duration were monitored using a fast *ITT* biplanar photodiode *(F-4014)* which sampled a portion of the light at 90° to the laser axis using a quartz beam splitter. Results were normalized and made quantitative on a routine basis using this diode. The laser excitation pulse and the xenon analyzing light are arranged in a crossed-beam manner intersecting in a quartz optical cell of 10×10 mm cross-section. The probed sample volume has dimensions of 5 mm by 3 mm diameter and is situated just inside the cell wall incident to the laser pulse.

Kinetic absorption spectrophotometry [15] of the generated transients was observed using a high intensity *Bausch & Lomb* monochromator coupled with a *R.C.A.* 1P28 or *EMI* 9785B photomultiplier and associated circuitry (overall risetime <1 ns). The electrical signal from the photomultiplier was either displayed on a *Textronix* oscilloscope *(7834-400MH$_2$)* or directly processed by a *Tektronix* transient digitizer *(R-7912-500MH$_2$)* into digital format for subsequent spectral and kinetic analysis on a *HP-9825A* calculator.

Actinometry of the transients was based upon pyrene in cyclohexane. The T-T spectrum of pyrene was monitored at 412 nm (using narrow slits and low laser intensity), taking $\varepsilon_{412} = 3.04 \times 10^4 \text{M}^{-1}$ cm^{-1} [10] and $\Phi_{\text{isc}} = 0.28$ [16].

The extinction coefficient of the triplet PTHDS was determined by triplet energy transfer. For this purpose, naphthalene, which has a triplet energy of 2.64 eV, served as an energy acceptor. A value of $\varepsilon_{413} = 2.45 \times 10^4 \text{M}^{-1}\ \text{cm}^{-3}$ was used for the triplet extinction coefficient.

Light-scattering measurements were made using a low-angle scattering photometer supplied by *Chromatix (KMX-6)*. The molecular weight determination of the scattering aggregates was obtained by measuring the excess *Raleigh* factors of the micellar solutions to that of water. The intensity fluctuations of the scattered light were used to determine the radii of the aggregates using a *Ford*-designed autocorrelator (resolution 0.1 μs, 64 channels). For these measurements the photomultiplier voltage was set at *ca.* 1300 V.

Fluorescent lifetimes were determined by the time-correlated single photon method [17]. The system was supplied by *P.R.A.* using a thyratron-triggered flash lamp source and *Ortec* detection electronics.

Surface tension measurements of the PTHDS solutions were accomplished by the *Wilhelmy* plate method at 25°. A *Kyowa* electro-surface balance was used for this purpose.

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