also causes the surface area of the lecithin molecule to increase. However, because of the approximations introduced in the T_1 calculation, it is not practical to draw any detailed quantitative conclusions about the apparent size change of the lecithin molecule from the empirical parameters used in the present calculation.

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Laser Photoionization of Phenothiazine in Alcoholic and Aqueous Micellar Solution. Electron Transfer from Triplet States to Metal Ion Acceptors

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Abstract: The 347.1-nm laser photolysis of phenothiazine (PTH) was studied in methanolic and aqueous sodium lauryl sulfate micellar solutions. Photolysis in both systems resulted in cation (PTH^+), solvated electron, and triplet (PTH^T) formation. Photoionization occurred via a monophotonic process and was much larger ($\Phi \approx 0.5$) in the micellar as compared to methanolic ($\Phi \approx 0.1$) solutions, whereas the PTH^T yields were smaller in the micellar as compared to the methanolic solutions. Efficient electron transfer was found to occur from PTH^T to metal ions such as Eu^{3+} and Cu^{2+}. Electron transfer rate constants in methanol for Cu^{2+} and Eu^{3+} were 6×10^9 and 4.7×10^9 M^{-1} sec^{-1}, respectively. Quenching of PTH^T by Mn^{2+} ions occurs at a much slower rate of 8×10^7 M^{-1} sec^{-1} and does not produce chemical change. Electron transfer occurs also from PTH^T solubilized within the micelles to Cu^{2+} and Eu^{3+} adsorbed on the micellar surface. The specific rate of this process is considerably larger than in homogeneous methanolic solutions.

Investigations of photoionization processes have recently become an important domain of photochemical research. Such reactions have been examined in various polar and apolar liquids.[1] Photoionization processes also play a major role in photobiology, a well-known example being the light reaction in chloroplasts during photosynthesis.[2] Pertinent features of such photoevents occurring in bioaggregates may be explored by means of micellar model systems.[3] In earlier studies polycyclic aromatic hydrocarbons incorporated into micellar assemblies were used as photoactive probes.[4,5] These were ionized by two photons of 347.1-nm laser light. Reactions of photoelectrons as well as parent cations, in particular the formation and behaviour of hydrated electrons, were examined in detail.[5] These investigations are now extended to hydrophobic probes, notably *N*-heterocyclics, which have exceptionally low ionization potentials and may therefore be ionized by one 347.1-nm photon. It is attempted to elucidate the role of anionic micelles in enhancing ion formation during the photolysis events. A further goal of our studies is to explore probes which in micellar systems can be ionized efficiently by visible light. The prospect exists of exploiting these systems for conversion of solar energy into hydrated electrons or hydrogen.

The present paper reports on the photochemical beha-

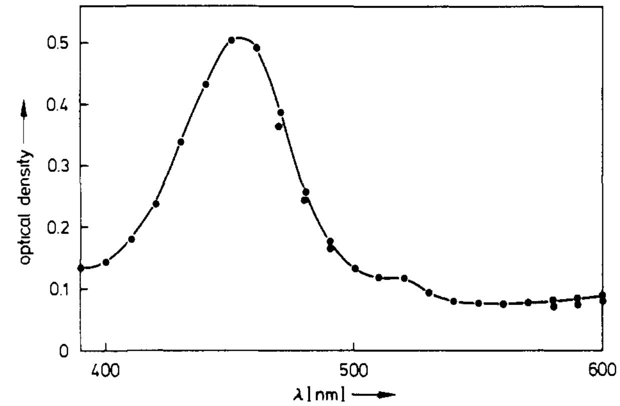


Figure 1. Transitory spectrum obtained from the laser photolysis of 5 × 10^{-5} *M* PTH in MeOH, deoxygenated.

viour of phenothiazine in methanolic and aqueous micellar solution. This probe was selected because of its low gas phase ionization potential[6] and its strong hydrophobicity which guarantees incorporation into the micellar aggregates. The ease of ionization has been attributed to the presence of two heteroatoms leading to a number of π electrons greater than $4n + 2$.[7] An important feature of this work is the study of a new type of light-initiated redox reaction which has not been observed previously. It will be shown presently that phenothiazine triplets readily transfer electrons to metal ion acceptors provided the reduction potential of the latter is favorable for this reaction.

Experimental Section

Materials. NaLS (sodium lauryl sulfate), Merck, was purified by numerous recrystallizations from methanol. Phenothiazine (Materials Ltd., Englewood Cliffs, N.J.) was zone refined. All other compounds were analytical reagent grade. Water was triply distilled.

Sample Preparation. Phenothiazine was solubilized in 0.1 *M* NaLS by gently stirring the mixture at 50-70°C. Care was taken to exclude light. The concentrations of solubilized phenothiazine were determined by spectrophotometric measurements. If necessary the samples were deoxygenated by bubbling with highly purified argon.

Apparatus. Laser photolysis experiments were carried out using a Q switched Korad K1QP ruby laser. The 347.1-nm pulse had a duration of 15 nsec and maximum energy of 100 mJ as measured by a bolometer. Transient species were detected by fast kinetic spectroscopy. A detailed description of this setup has been published elsewhere.[8] Suitable cut-off filters were placed in the analyzing light beam to avoid photolysis. Solutions were flowed through a 1 cm^2 quartz cell avoiding interference from product accumulation.

Results and Discussion

(I) Laser Photolysis of Phenothiazine in Methanol. The transitory spectrum obtained with a solution of 5 × 10^{-5} *M* phenothiazine immediately after the laser pulse is shown in Figure 1. It is dominated by a strong absorption which peaks around λ 460 nm. One notices also a hump at 520 nm and a band rising toward the red at λ >560 nm. The latter is removed by typical electron scavengers such as N_2O or NO_3^- and is therefore attributed to solvated electrons (e_s^-). Available literature evidence suggests that the other two bands at 520 and 460 nm originate from phenothiazine cation radicals (PTH^+)[9] and triplets (PTH^T),[7,10,13] respectively.

These assignments are substantiated further by scavenging and quenching experiments. Saturation of methanol with oxygen, for example, removes the 460-nm absorption; OH^-, on the other hand, affects only the decay kinetics of the species with λ_{max} 520 nm. From such experiments one can also distinguish the OD contributions of each of the three transients to the total optical density at a given wavelength:

$$OD_\lambda = OD_\lambda(e_s^-) + OD_\lambda(PTH^+) + OD_\lambda(PTH^T) \qquad (1)$$

The yield of solvated electrons calculated from OD_{600} (e_s^-) and the extinction coefficient[11] of e_s^- was found to increase linearly with the laser intensity. This suggests that ionization of PTH in methanol, similar to acetonitrile solutions,[12] occurs via a monophotonic mechanism.

$$PTH \xrightarrow{h\nu} PTH^+ + e_s^- \qquad (2)$$

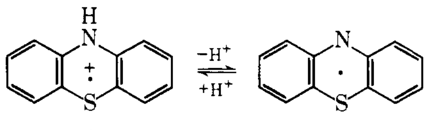
The quantum yield for this process is $\Phi \approx 0.1$ and was obtained from the absorbance of a 5 × 10^{-5} phenothiazine solution at λ 347.1 nm, the number of photons per pulse and an effective irradiated volume of 1 cm^3. As the irradiated volume cannot be measured precisely the quantum yields determined by this procedure are subject to relatively large errors. With the knowledge of the concentration of e_s^- and therefore [PTH^+] one can evaluate the extinction coefficient of phenothiazine cation radicals: $\epsilon_\lambda(PTH^+) = OD_\lambda(PTH^+)/[PTH^+]$.

For λ_{max} 520 nm one obtains:

$$\epsilon_{max}(PTH^+) = 9.3 \times 10^3\ M^{-1}\,cm^{-1}$$

This value may be compared to $\epsilon_{max}G = 4100$ obtained from pulse radiolysis of PTH in chloroform.[13] (The radiation chemical yield $G(PTH^+)$ was not determined in these experiments.)

The principal reaction of PTH^+ in methanolic solution is rapid recombination with e_s^- with a first half-lifetime of several hundred nanoseconds. If an electron scavenger is added to the solution the lifetime of PTH^+ increases to about 3 μsec. Under such conditions it disappears via loss of a proton yielding the neutral radical PT.



(3)

In the presence of water the rate of reaction 3 increases which is probably due to the stronger proton affinity of H_2O as compared to CH_3OH. A rate constant for the proton transfer reaction $k_{PTH^+ + H_2O} = 6.8 \times 10^5\ M^{-1}\ sec^{-1}$ was obtained from the enhanced rate of positive ion decay.

As was mentioned above the 347.1-nm photolysis of phenothiazine in methanol produces, apart from e_s^- and cation radicals, phenothiazine triplets. It is instructive to examine the behavior of the latter species in more detail. In deaerated methanol the triplets disappear via mixed first- and second-order kinetics with a first half-lifetime of 6 μsec. The lifetime is greatly reduced in the presence of various metal ions indicating efficient quenching of the triplets.

During the course of these investigations it was discovered that the quenching process occurs via electron transfer from the phenothiazine triplets to the metal ions:

$$PTH^T + M^{n+} \longrightarrow PTH^+ + M^{(n-1)+} \qquad (4)$$

An illustration of this reaction is given in Figure 2 which shows oscillograms obtained from the laser photolysis of phenothiazine in methanol containing 3 × 10^{-3} *M* $Eu(NO_3)_3$. The optical density at λ 460 and 520 nm increases during the laser pulse reflecting the formation of triplets and positive ions. (Solvated electrons are scavenged rapidly by nitrate anions and hence do not contribute to the transient absorption. The optical signal at 460 nm where PTH^T has maximum absorption decreases rapidly after a few hun-

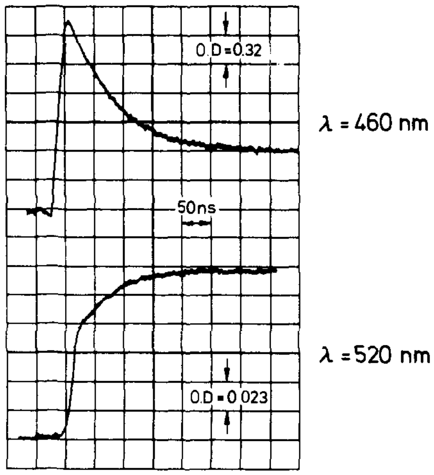


Figure 2. Oscilloscope traces showing PTH^T decay (upper trace) and the PTH^+ formation (lower trace) during the laser photolysis of 5×10^{-5} *M* PTH in MeOH containing 3×10^{-3} *M* $Eu(NO_3)_3$.

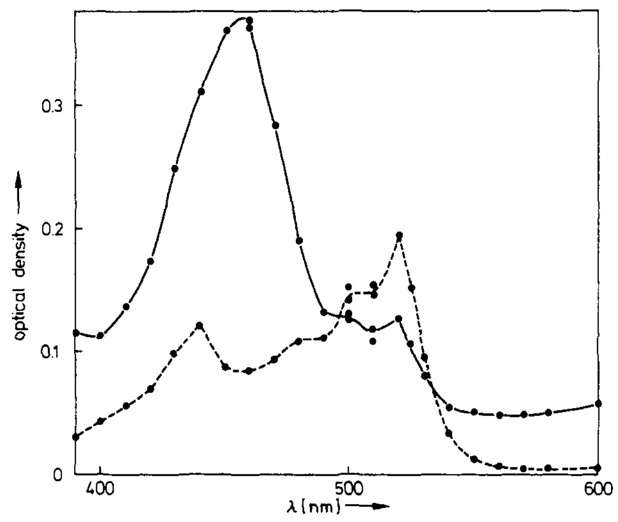


Figure 3. Transitory spectra obtained from the laser photolysis of 5×10^{-5} *M* PTH in deoxygenated methanol solution containing 3×10^{-3} *M* $Eu(NO_3)_3$. Solid line: spectra immediately after the pulse. Dashed line: spectra 300 nsec after the pulse.

Table I. Quenching of Phenothiazine Triplets (PTH^T)

Solute(s)	k_{s+PTH^T}, M^{-1} sec^{-1} [a]	$1/\tau$, sec^{-1} [b]
O_2	2.4×10^{10} [d]	1.2×10^{7} [c,d]
Mn^{2+}	8×10^{7} [d]	1.1×10^{6} [d]
Eu^{3+}	4.7×10^{9} [e]	1.9×10^{7} [e]
Cu^{2+}	6.0×10^{9} [e]	3.6×10^{7} [e]

[a] 5×10^{-5} *M* PTH in methanol. [b] 5×10^{-5} *M* PTH in aqueous 0.1 *M* NaLS: $[M^{n+}] = 3 \times 10^{-3}$ *M*. [c] O_2 saturated. [d] No electron transfer observed. [e] Electron transfer quenching.

dred nanoseconds until a plateau is attained. Conversely, at 520 nm, the wavelength of the PTH^+ absorption maximum, the OD increases further after the pulse until a final level is reached. The kinetics of the 520-nm growth match those of the 400-nm decay indicating the formation of PTH^+ during the reaction of Eu^{3+} with PTH^T. Apparently the quenching process involves electron transfer from phenothiazine triplets to europium ions. This conclusion is substantiated by examining the transitory spectrum after completion of the triplet decay, Figure 3. The spectrum is identical with that of phenothiazine cation radicals, the yield of the latter being much larger that that observed in Eu^{3+} free solution. Oscilliscope traces such as Figure 2 can be described by first-order kinetics, plots of ln OD vs. time yielding straight lines. From the slopes, which increase linearly with Eu^{3+} concentration, one obtains a value for the bimolecular rate constant of the redox reaction (4)

$$k_4(Eu^{3+}) = 4.7 \times 10^9 \ M^{-1} \ sec^{-1}$$

In order to examine the influence of the standard potential of the redox couple $M^{n+}/M^{(n-1)+}$ on reaction 4, experiments were performed using several other metal ions as triplet quenchers. These data are listed in Table I. Cu^{2+} ions are also reduced by phenothiazine triplets, the rate constant being 6×10^9 M^{-1} sec^{-1}. The difference in the $k_{Cu^{2+}+PTH^T}$ and $k_{Eu^{3+}+PTH^T}$ values, although small, nevertheless exceeds distinctively the error limit for these rate constants which is about 5%. The rate of electron transfer to Cu^{2+} may be enhanced by the higher electron affinity of Cu^{2+} ($E_0 = 0.158$ V) as compared to Eu^{3+} ($E_0 = -0.4$ V). Alternatively as both values are close to diffusional rates diffusional effects rather than E_0 values could well determine only small differences in the quenching rate constant. Mn^{2+} ions on the other hand are not reduced by PTH^T. The quenching process in this case probably involves paramagnetic enhancement of radiationless deactivation to the ground singlet state. It occurs with a rate constant which is typical for the quenching of aromatic hydrocarbon triplets by paramagnetic metal ions.[14] Apparently the reduction potential of Mn^{2+}, $E^0(Mn^{2+}/M^{1+}) \simeq -3$ V,[15] is too negative making reaction 4 energetically unfavorable. The fact that electron transfer quenching is faster for Cu^{2+} than for Eu^{3+} ions while it does not occur in the case of Mn^{2+} indicates that the standard potential of the $M^{n+}/M^{(n-1)+}$ redox couple may be used as a guide for the efficacy of this process. Comparison of $E^0(Eu^{3+}/Eu^{2+}) = -0.4$ V and $E^0(O_2/O_2^-) = -0.3$ V [16] would indicate that oxygen might also be a candidate for phenothiazine triplet quenching via electron transfer. Triplet lifetime measurements in aerated and oxygenated methanol solution showed that the quenching process indeed occurs with an extremely fast rate, Table I. However, no evidence was found for electron or hydrogen transfer from PTH^T to O_2. The spectrum observed after completion of the triplet decay is identical with that of PTH^+, the yield of cation radicals being the same as in oxygen-free solution. This excludes electron or hydrogen transfer as the dominant quenching mechanism (hydrogen transfer leads to the unprotonated form of PTH^+ which has a characteristic absorption band at $\lambda < 430$ nm).

Hydrogen transfer from PTH^T to oxygen occurs with a relatively small yield in ethanol[10] and other organic solvents.[17] It has been shown that quenching of hydrocarbon triplets occurs via energy transfer producing singlet oxygen.[18] It is suggested that a similar mechanism is operative here which would account for the extremely rapid quenching rate.

The possibility of converting phenothiazine triplets into cation radicals via electron transfer reactions can be utilized to determine the quantum yield of triplet formation and the PTH^T extinction coefficient which is not available in the literature. As the formation of PTH^+ and the disappearance of PTH^T occur at the same rate a significant contribution of processes other than reaction 4 to the triplet anihilation can be excluded. Hence it can be assumed that conversion of PTH^T into PTH^+ by ions such as Eu^{3+} is quantitative. The amount of triplets formed during the laser photolysis is then calculated from the difference of cation radical yield obtained in solutions with and without Eu^{3+} ions

$$[PTH^T] = (OD_{520}'(PTH^+) - OD_{520}(PTH^+))/\epsilon$$

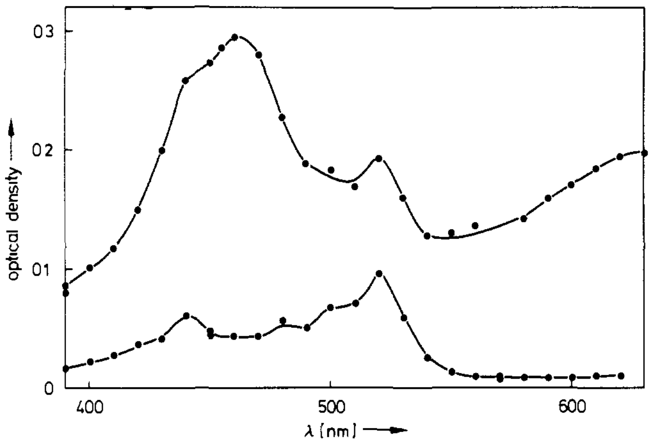


Figure 4. Transitory spectra obtained from the laser photolysis of 5 × 10^{-5} *M* PTH in 0.1 *M* NaLS. Upper curve: spectra immediately after the pulse in deoxygenated solution. Lower curve: spectra 400 nsec after the pulse in oxygen saturated solution.

where $OD'_{520}(PTH^+)$ and $OD_{520}(PTH^+)$ denote the contributions of PTH^+ to the optical density at 520 nm a few hundred nanoseconds after the laser flash in the presence and absence of Eu^{3+} ions, respectively, and ϵ is the extinction coefficient of PTH^+. One evaluates that the amount of phenothiazine triplets is six times greater than that of cation radicals or solvated electrons. Hence $\phi\ (PTH^T) \approx 0.6$.

The value for the extinction coefficient of phenothiazine triplets obtained from $OD_{460}(PTH^T)$ and the triplet concentration is

$$\epsilon_{460}(PTH^T) = 2.7 \times 10^4\ M^{-1}\ cm^{-1}$$

It is concluded that the principal pathway of PTH photolysis in methanolic solution leads to triplet formation, the photoionization channel having only minor significance. However, as phenothiazine triplets have strongly reducing properties, the photolysis events may change completely if electron affinic substances are present in the solutions. In this case ionization of phenothiazine and simultaneous reduction of the acceptor are the prominent photoreactions. It is important to note that one deals here with a rather unique redox reaction involving triplet states as reductant of simple metal ions which hitherto has not been observed. With the knowledge of the photochemical behavior of phenothiazine in a pure solvent we now procede to examine the course of photolysis events for a situation in which the same probe is embedded in the hydrocarbon microphase of a micellar aggregate.

(II) Laser Photolysis of Phenothiazine in Aqueous Micellar Solution. In aqueous micellar sodium lauryl sulfate (NaLS) solution, phenothiazine due to its hydrophobic nature is dissolved almost quantitatively in the apolar interior of the micelles. This is indicated by the fact that hydrated electrons (e_{aq}^-) produced in a photolysis or pulse radiolysis experiment decay with the same rate in PTH-free or PTH-containing NaLS solutions. If a substantial fraction of PTH were located in the aqueous bulk phase, the e_{aq}^- decay would be enhanced, since PTH is reduced by solvated electron with a diffusion-controlled rate constant of 3 × 10^9 M^{-1} sec^{-1}. PTH located within NaLS micelles on the other hand is protected from e_{aq}^- attack by the repulsive micellar negative surface potential.[19]

Transitory spectra obtained from the laser photolysis of PTH solubilized in NaLS micelles are shown in Figure 4. The upper spectrum is observed in a deoxygenated solution immediately after the laser pulse. Similar to the methanol spectrum it contains the peaks for triplets and cation radicals at 460 and 520 nm, respectively, and the absorption band of e_{aq}^- rising toward the red. However, the relative proportions of the PTH^+ and e_{aq}^- to triplet absorption are comparatively much larger than those in methanol indicating a higher yield of photoionization in the micellar solution. The lower spectrum was taken in oxygenated NaLS solution at a time where PTH^T and e_{aq}^- have disappeared by reaction with oxygen (~400 nsec). It shows maxima at 440 and 520 nm and is identical with the PTH^+ literature spectrum.[9]

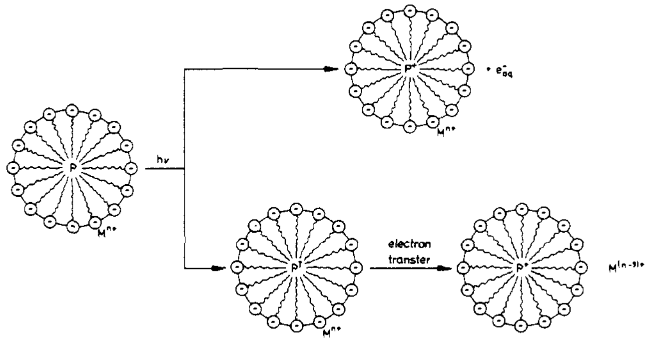


Figure 5. Schematic representation of photoionization and electron transfer processes in solutions of surfactant micelles containing a solubilized photoactive probe P. The electron acceptor is M^{n+} located in the Stern layer of the micelle and the electron is transferred through the Stern layer from the triplet (P^T).

From these data it can be inferred that photoionization and triplet formation are the only primary steps in the 347.1-nm photolysis of phenothiazine in NaLS micellar solution:

$$(PTH)_M \xrightarrow{h\nu} \begin{cases} (PTH^+)_M + e_{aq}^- & (5a) \\ (PTH^T)_M & (5b) \end{cases}$$

The subscript M denotes association with the micellar phase. The yield of photoionization as determined from $OD_{600}(e_{aq}^-)$ and the extinction coefficient for hydrated electrons at 600 nm was found to increase linearly with the laser intensity indicating a monophotonic process. From a calculation analogous to that described in the previous section one derives $\phi\ (e_{aq}^-) \approx 0.5$ and for the extinction coefficient of the phenothiazine cation radicals in the micellar environment at λ_{max} 520 nm

$$\epsilon(PTH^+)_M = 6.3 \times 10^3\ M^{-1}\ cm^{-1}$$

It was already pointed out earlier[4,5] that hydrated electrons produced bv the photoionization process 5a cannot reenter the micelle and recombine with parent cations. The most likely fate of e_{aq}^- in micellar solution is conversion into H_2 via the bimolecular reaction:

$$e_{aq}^- + e_{aq}^- \longrightarrow 2OH^- + H_2 \qquad (6)$$

which occurs with a rate constant[20] of 6 × 10^9 M^{-1} sec^{-1}.

Concentrations of hydrated electrons achieved from the photolysis of 5 × 10^{-5} *M* solutions of phenothiazine in 0.1 *M* NaLS are ≤3 × 10^{-5} *M*. From k_6 one calculates for the first half-lifetime of the hydrated electron decay $\tau_{1/2} \geq 5$ μsec which is in agreement with the experimental observation.

In NaLS micellar solution the lifetime of phenothiazine cation radicals is much longer than in methanol. The decay of the 520-nm absorption occurs here over a period of several milliseconds and leads to the formation of a stable product with a spectrum shown in Figure 5. This spectrum is readily identified with that of phenothiazine radicals (PT)

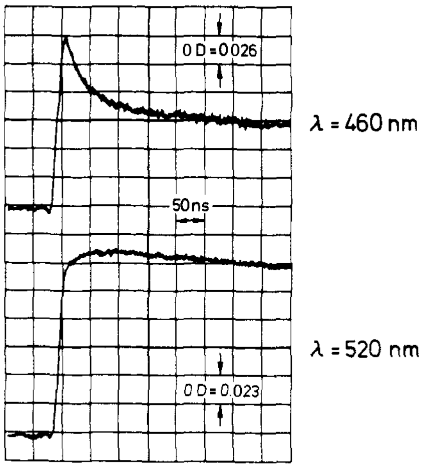


Figure 6. Oscilloscope traces showing PTH^T decay (upper trace) and the PTH^+ formation (lower trace) during the laser photolysis of 5×10^{-5} M PTH in 0.1 M NaLS containing 3×10^{-3} M $Eu(NO_3)_3$, deoxygenated.

originating from deprotonation of PTH^+ according to eq 3. PT radicals are known to be very stable existing for hours or days in solution.[9,10,21] As the deprotonation in the aqueous bulk phase occurs within a few microseconds the rate-determining step in the annihilation of PTH^+ must be its exit from the NaLS micelle. It is concluded that PTH^+ leaves the micellar interior, where it is originally formed, with a relatively slow rate. A similar behavior has been found for pyrene cation radicals.[4,5] The formation of PT via deprotonation of PTH^+ can be prevented by lowering the pH of the solution. For example at pH <4 no decay of PTH^+ absorption is observed on a millisecond time scale indicating thermodynamic stability of PTH^+ if $[H^+] > 10^{-4}$ M. From these observations one derives a pK value between 4 and 5 for the phenothiazine cation radicals in aqueous NaLS solution.

Similar to PTH^+ the phenothiazine triplets are much more long lived in the micellar than in the methanolic solution. The triplets decay with a first lifetime of 300 to 500 μsec depending on the laser dose. The increase in the triplet lifetime is caused by slow exit of PTH^T from the micelles and micellar inhibition of triplet-triplet annihilation. A detailed dicussion of these phenomena has been given elsewhere.[19]

The fact that phenothiazine triplets reside in the micelles for a period of several hundred microseconds favors an investigation of electron transfer processes from PTH^T to acceptors located in the aqueous phase or adsorbed within the micellar Stern layer. The latter situation is of particular interest since a study of this type of reactions might enlighten us as to the nature of electron transport processes across charged lipid water interfaces. In the following we will use Mn^{2+}, Eu^{3+}, and Cu^{2+} as triplet quenchers. Their reactions with PTH^T in alcoholic solutions were scrutinized in the preceding section. The pecularity of the situation encountered in anionic micellar systems lies in the fact that multiply charged positive metal ions are strongly adsorbed on the surface of the aggregates.[5,22] It ensues that the electron transfer reaction in micellar systems, in contrast to the alcoholic solutions, is not a bimolecular process obeying homogeneous second-order kinetics. It rather has to be regarded as a summation of intramicellar events occurring between single donor acceptor pairs. Such a reaction is expected to obey first-order kinetics, the rate depending on the degree of covering of the micelle by the acceptor ions and the efficiency of electron transport through the micelle-water interface. Figure 6 illustrates the pathway of phenothiazine photolysis in solutions of anionic micelles in the presence of adsorbed metal ion acceptors. The absorption of light primarily leads to formation of e_{aq}^-, PTH^+, and PTH^T. Subsequently electrons are transferred from phenothiazine triplets across the micellar Stern layer to the adsorbed metal ions.

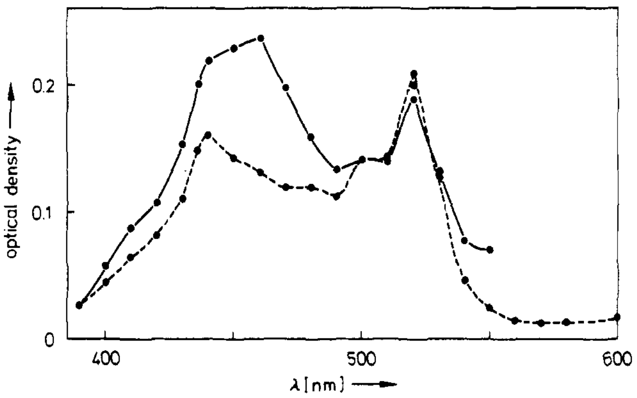


Figure 7. Transitory spectra obtained from the laser photolysis of 5×10^{-5} M PTH in deoxygenated 0.1 M NaLS solution containing 3×10^{-3} M $Eu(NO_3)_3$. Solid line: spectra immediately after the pulse. Dashed line: spectra 100 nsec after the pulse.

Oscilloscope traces showing the optical events at λ 460 and 520 nm during the laser photolysis of PTH in micellar NaLS containing Eu^{3+} ions are presented in Figure 7. A very rapid decay of the PTH^T absorption at 460 nm is observed which partially occurs already during the laser pulse. The concomitant formation of PTH^+ via reaction 4 is noticeable at 520 nm. A kinetic analysis of these curves was carried out by plotting log [OD(t) − OD(p)] vs. time. OD(p) is the optical density change in the plateau region after completion of the triplet decay. The semilog plots yield straight lines indicating the first-order character of the electron transfer reaction. Rates for this process may be best expressed by reciprocal triplet lifetimes and are listed for Eu^{3+}, Cu^{2+}, and Mn^{2+} ions in Table I. Analogous to the results obtained with alcoholic solutions, the former two ions quench phenothiazine triplets very efficiently and via electron transfer, while Mn^{2+} reacts at a much slower rate via enhancement of PTH^T radiationless deactivation. Clearly the Mn^{2+} reduction potential is too negative to allow for occurrence of electron transfer from PTH^T. In this context it is interesting to note that silver ions adsorbed on the surface of NaLS micelles are capable of oxidizing ground state PTH to PTH^+. If Ag^+ is added in the dark to an NaLS solution of phenothiazine one observes immediate formation of PTH^+. Apparently in this system the redox potential $E_0(Ag/Ag^+)$ is more positive than $E_0(PTH/PTH^+)$: 0.8 V $> E_0(PTH/PTH^+)_{NaLS}$. The oxidation potential of PTH in pure aqueous solution is expected to be several hundred millivolts more positive than this value corresponding to the potential difference between micellar interior and aqueous phase.

The extremely rapid nature of the electron transfer from PTH^T within the micelle to adsorbed Eu^{3+} and Cu^{2+} ions requires further consideration. As the microviscosity prevailing in the micellar interior is 30 times greater than that of a liquid hydrocarbon[23] the time required for a hydrophobic probe to diffuse from the micellar center to the periphery region is expected to be about 80 nsec. Even if one concedes that PTH due to its hydrophilic NH group is located in the outer core region of the micelle and hence can reach the surface more rapidly the fact remains that only a negligibly small fraction of the Stern layer is occupied with acceptor metal ions. (The average number of ions per micelle

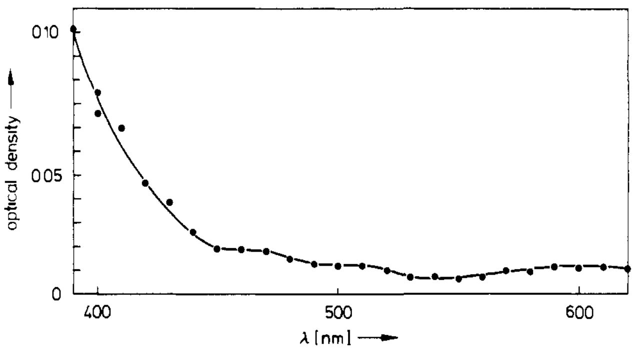


Figure 8. Spectra of PT observed 10 msec after the laser pulse in 5×10^{-5} *M* PTH in 0.1 *M* NaLS, deoxygenated.

is two under our conditions.) If the redox reaction would procede through the stage of a collisional complex between the two reactants then its rate should be relatively slow since encounters between PTH^T and M^{n+} are improbable. In fact it has been shown previously that diffusion-controlled intramicellar electron transfer requires a time period of more than 10^{-6} sec.[5] A large number of electron,[24] charge transfer,[25] and electrode[26] reactions on the other hand occur via tunneling of the electrons. In particular the work by Kuhn[27] on photoejection of electrons from chromophores embedded into lipid monolayers has established the occurrence of tunneling of photoexcited electrons through distances of 10 Å and more within the lipid phase. By analogy with the latter systems it seems reasonable to postulate that electrons can tunnel from the PTH^T donor located within the micellar hydrocarbon phase through the micellar Stern layer to the site of the acceptor in the aqueous phase. The probability of these processes will depend on the height of the energy barrier and the overlap of electronic levels of the two reactants. These phenomena will be dealt with in a subsequent paper.

Similar to the alcoholic solutions the quantitative conversion of PTH^T into PTH^+ can be shown by examining the transitory spectra immediately and a few hundred nanoseconds after the laser pulse. The end of pulse spectrum in Figure 7 resembles the upper curve of Figure 8 and hence contains significant contributions from PTH^T. After completion of the triplet decay the spectrum is identical with that of PTH^+, the yield of the latter being significantly larger than in Eu^{3+} free solution. This increase of $OD_{520}(PTH^+)$ allows the calculation of the amount of triplets formed by the laser pulse as well as the PTH^T extinction coefficient in the micellar microenvironment. One obtains from a procedure analogous to that described in the preceding section: $\Phi(PTH^T) \approx 0.3$ and $\epsilon_{460}(PTH^T) = 2.2 \times 10^4\ M^{-1}\ cm^{-1}$.

A comparison of triplet and photoionization yields in the micellar and alcoholic system reveals the interesting fact that both magnitudes are interrelated. The smaller the ionization the higher the triplet yield. This finding could be explained in the terms of a common source of the two photolysis channels represented by a highly excited state which either ionizes or relaxes to give a triplet state. Such a mechanism has been shown to be operative in the photolysis of indole derivatives in aqueous solution.[28] If the highly excited states are formed in a negatively charged micelle, photoejection could occur via tunneling of the photoelectron through the micellar double layer into the potential traps of the surrounding aqueous phase. Such a process is enhanced by the negative potential in the micelle and on the micellar surface which also inhibits recombination of geminate ion pairs. The latter factors which promote ionization are absent in alcoholic solution. Even if the initial photoejection occurred here with the same probability as in the NaLS micelles ion pairs could recombine, a reaction, which is a possible source of the high triplet yield found for phenothiazine in methanol.

Conclusion

Laser photolysis (347.1 nm) of phenothiazine in NaLS micellar and methanolic solution leads to formation of solvated electrons, cation radicals, and triplets, the yield of ions being much larger in the micellar than in the methanolic system. Cation radicals are also produced by electron transfer from phenothiazine triplets to suitable metal ions. It is feasible to utilize the latter reaction in a photo galvanic cell. The advantages of the phenothiazine-NaLS-M^{n+} system follow. Metal ion reduction occurs with a quantum yield of almost unity. The phenothiazine cation radical produced in the primary photolysis step is unusually long lived allowing for electrical regeneration of PTH. Further stabilization may be achieved by using N-substituted phenothiazines. The PTH absorption spectrum extends into the visible and may be red shifted further by substitution. This would possibly allow for exploitation of solar light energy. As an extension of these studies similar types of light-initiated redox reaction are presently being investigated with other electron acceptors, in particular quinone derivatives, and the investigations are extended to aggregates such as phospholipid vesicles which have greater biological relevance. From such experiments further insight is expected into light-induced redox processes occurring in vivo such as chlorophyll oxidation during photosynthesis.

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Studies of Membrane Processes. VII. Hydrocarbon Chain Motions and the Effect of Changing Counterions

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Abstract: A number of specifically deuterated decylsulfates and decanols have been prepared and used as components of lyotropic nematic phases. The deuterium magnetic resonance spectra of these phases are a series of doublets arising from partially averaged nuclear quadrupole couplings. By preparing similar phases, but with enrichment in decylsulfate or decanol or both, the doublets can be assigned to specific methylene groups in the chains. While the results are similar to recent results in other detergent and phospholipid bilayer systems, indicating the same general behavior of these membranoid systems, there are significant and interesting differences. A pronounced alternating orientation effect near the ionic head group is assigned to structural effects of the electrical double layer interface which causes preferential formation of kinks at certain carbons more than others near the head group. The region of approximately constant degree of orientation from positions 1 to 8 is less extensive than in longer chain phospholipid systems but is still present and represents a region of kink equilibrium affecting all carbons equally. The fall off in degree of order at the chain ends is analyzed in terms of rotations about the 8,9 or 9,10 carbon-carbon bonds. The decanol chains are considerably more highly ordered than the decylsulfate chains except at the last carbon. This shows that the flexibility of hydrocarbon chains is a function of the head group and that the chains of the bilayer, although ordered much more than in a hydrocarbon solution, do still act as a heterogeneous two-dimensional ordered solution in these phases, rather than a one-component homogeneously ordered system. The chain flexibility is a function of the counterion even down to the free end of the chain. From the changes in ratios of quadrupole splittings with the counterion it is shown that in the series NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, and $(CH_3)_4N^+$, it is the dimethylammonium ion which has more ability to penetrate and build structure in the electrical double layer interface. Increase in interface order with counterion can be expressed in the following way: $(CH_3)_2NH_2^+ > (CH_3)_3NH^+ \sim CH_3NH_3^+ > NH_4^+ \sim (CH_3)_4N^+$.

Several recent papers and communications[1-12] have described the application of the nuclear magnetic resonance (NMR) tool to lyotropic liquid crystal systems which are homogeneously oriented in the magnetic field. There is a lack of low-angle X-ray diffraction data for the particular systems we have studied and none at all for nematic samples oriented by magnetic fields.[13-16] In these recent papers a superstructure array of infinitely long cylinders of the middle step nematic type have been implicitly assumed, but some results obtained are difficult to explain in this model.[10] Ultimately this lack of knowledge of the exact superstructure array is not a serious handicap in probing the nature of the electrical double layer and hydrophobic regions of the phases at the molecular and ionic level.[8] The lipid bilayer matrix associated with most models of the biological membrane is a close relative of the detergent bilayer and other superstructure arrays of lyotropic liquid crystals.[17] The detergent bilayer system is simpler than the branched chain lipid systems,[18] but the NMR results reported for both types of bilayer are remarkably similar.[8,19-22] The same basic processes can be studied in both models[23] and these processes are common to all bilayer membranes. It is this feature which attracts our attention, while separately we have also been successful in orienting complex ions and have determined some ion structures.[2,5,6,8,11,12,24]

The thermotropic liquid crystal is such that each molecule of a one-component phase is aligned in a statistically equivalent manner.[25] The heterogeneity of statistical ordering of the microcomponents that make up lyotropic nematic phases is an interesting problem and some work in this field has appeared.[1,7,8,10,16] The division of these lyotropic nematic phases into the hydrophobic, electrical double layer, and hydrophilic regions provides us with a crude membrane model to study typical microprocesses at the level of ions, water, ionic head, or chain segment. In this particular study the preparation of specifically deuterated detergents is described and the lyotropic nematic phases made with these detergents are varied by changing the nature of the counterion. The changes in degree of microorder of various components of the phases are studied with a view to interpretation in terms of ion penetration. Deuterium magnetic resonance is the principal tool used to describe the degrees of order.

Experimental Section

Deuterium magnetic resonance spectra were obtained at ~27° from a Varian XL-100 spectrometer or a Bruker Hx-90 spectrometer both equipped with Fast Fourier Transform capability. (We are greatly indebted to Professor J. B. Stothers for obtaining the XL-100 spectra for us.) Spectral widths were between 10 and 20 kHz and pulse widths were 25 μsec. About 1000 transients of 8K data points were collected, processed to the frequency mode, then displayed on paper. Time between pulses was 0.3 sec. Noise decoupling of 1.5 kHz bandwidth at 100 MHz was employed to decouple the protons from the deuterium. This resulted in a considerable sharpening of the deuterium transitions but this gain was partially offset by the fact that the data were collected before the system obtained a high degree of homogeneity. Data collection was begun