Magnetic Relaxation in the Lecithin–D_2O System

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Abstract: The proton spin–lattice relaxation time (T_1) for lecithin in the lecithin–D_2O system was studied over the temperature range −65 to +70° and the frequency range 5.2 to 60.0 MHz. For oriented samples in the liquid crystalline phase, T_1 for "all protons" of the lecithin bilayers did not show an angular dependence with respect to the orientation in the magnetic field. It is therefore suggested that spin diffusion may not be the major relaxation mechanism for the methylene protons. When the temperature was lowered, T_1 for the methyl protons showed an inflection at the transition temperature from the lamellar to the gel phase (ca. 10°) and another inflection at ca. −35°. T_1 for the methyl protons is independent of the water concentration in the gel phase but decreases with the decrease of water concentration in the lamellar phase. Quantitative calculation on the methyl T_1 assuming a log-Gaussian distribution of the correlation time was performed, and the results agree well with the experimental data. The dependence of the methyl T_1 upon both temperature and concentration is related to the motion of the lecithin molecules in different phases.

The large number of nuclear magnetic resonance (NMR) studies on aqueous lecithin solutions in recent years has been primarily prompted by the general interest in the understanding of the structure and function of biological membranes. The phase diagram of the two-component water–egg yolk lecithin system has been studied in detail.[1,2] At low concentrations of lecithin, the system forms a true solution. From ca. 20 to 56% by weight of lecithin, the system forms two phases (liquid crystalline plus liquid) at ambient temperature. Above 56% of lecithin, the system forms a lamellar (multilayer) liquid crystalline phase at ambient temperature, which changes into a hexagonal (gel) phase when it is cooled. The transition temperature is dependent upon the concentration; it changes gradually from 5° for 56% lecithin to 40° for anhydrous lecithin. Sonification of dilute lecithin solutions produces bilayer vesicles which give rise to relatively sharp proton and ^{13}C NMR lines.[3-9] However, it has been demonstrated that real biomembranes show broad NMR absorptions;[1-12] therefore, it was suggested that liquid crystalline lipid solutions are better model systems in studying the structure and motion of biomembranes.[13]

Current NMR work in a number of laboratories has resulted in much interesting and useful knowledge on lecithin model membranes.[3-21] Some earlier controversies have been resolved by well-designed and careful experiments; other important discrepancies between different workers have remained unsettled. For example, the dependence of the ^1H NMR line width of lecithin multilayers on the magnetic field strength[8,12,19] was subjected to various interpretations until Feigenson and Chan[13] convincingly demonstrated that the effect was caused by the difference in the chemical shifts for different methyl and methylene groups. On the other hand, there is still no concensus to the mechanism responsible for the spin–lattice relaxation time, T_1, of the methyl and methylene protons.[7,13,14,16]

Unlike a nonviscous liquid, the spin–lattice relaxation time of many liquid crystalline and biological systems is strongly dependent upon the resonance frequency. In order to better understand the relaxation behavior of those systems, it is often necessary to conduct the T_1 measurement over large ranges of frequency and temperature. Previous relaxation studies on lecithin–water systems have been performed either at a single frequency or temperature, or over limited ranges of frequency and temperature.[13,14,16,21] Here we would like to report the proton T_1 in the egg yolk lecithin–D_2O system of different concentrations at five frequencies, ranging from 5.2 to 60 MHz, and over the temperature range of −65 to +70°. The experimental information is compared to theoretical calculations of T_1. To us, the results shed new light on the understanding of the magnetic relaxation of lecithin molecules in the crystalline, gel, and lamellar phases.

Experimental Section

Egg yolk lecithin was obtained from Sigma Chemical Co. It was dried at 50° under vacuum for 20 hr or more just prior to the preparation of samples each time. Deuterium oxide (D_2O) (99.7%) was obtained from Stohler Isotopes, Inc. Lecithin–D_2O samples were prepared by weighing out appropriate amounts of each component and mixed thoroughly by centrifuging back and forth through a narrow constriction in a sealed tube. Samples containing 58, 67, and 74% by weight of lecithin were studied. If the average molecular weight of egg yolk lecithin is taken as 763,[19,22] the D_2O–lecithin mole ratios in the samples were 28, 19, and 13, respectively.

Oriented lecithin multilayers were prepared by smearing liquid crystalline solutions of lecithin in D_2O on a thin glass plate, rubbing along one direction.[23] Glass plates (10–12) were stacked together for the NMR measurement. By examining samples prepared this way with a polarizing microscope, essentially complete orientation was ascertained.

Relaxation measurements were performed with a home-built pulsed NMR spectrometer equipped with a 12-in. high resolution magnet and a variable temperature probe by Bruker. Due to the small signal-to-noise ratio of the oriented samples, signal accumulations were made with a Nicolet 1070 signal averager. T_1 values were obtained by the 180°–τ–90° technique; the precision of individual T_1 measurements varied between 5% or less at high frequencies and temperatures to about 10% at low frequencies and temperatures.

Results and Discussion

The free induction decay (FID) signals of an ordered lecithin sample oriented at two different angles with respect to the magnetic field are shown in Figure 1. It is obvious that the dipolar interaction and, thus, T_2^* (apparent spin–spin relaxation time as determined from the FID) are dependent upon the orientation angle. However, the T_1's of the protons are independent of the angle of orientation within experimental error (Table I). This is an interesting result, since it casts serious doubt upon the argument that spin diffusion is the major relaxation mechanism[13,14,17,18] for the methylene protons in lecithin. It has been shown, both theoretically and experimentally, that T_1 due to spin diffusion is strongly dependent upon the angle between the magnetic field and the vector joining the fast relaxing center and the spin concerned.[24,25] Although T_1 for the methylene protons in lecithin cannot be determined separately, the T_1 data for "all"

Table I. Proton T_1[a] (sec) for Oriented Lecithin Samples at Various Angles between the Glass Plates and the Magnetic Field

			0°	30°	60°	90°	120°	150°	180°
Sample I,[b]	45°	"All protons"	0.181	0.170	0.173	0.182	0.183	0.183	0.183
	60 MHz	Methyl	0.227	0.234	0.238	0.226	0.238	0.238	0.236
Sample II,[c]	24°	Methyl	0.106	0.103	0.106	0.104	0.110		0.104
	20 MHz								

[a] Experimental error, ±5%. [b] Sample prepared from a mixture containing 65% lecithin. [c] Sample prepared from a mixture containing 74% lecithin. It should be noted that the lecithin concentrations might have increased slightly due to evaporation of D_2O in the process of preparing the glass plates.

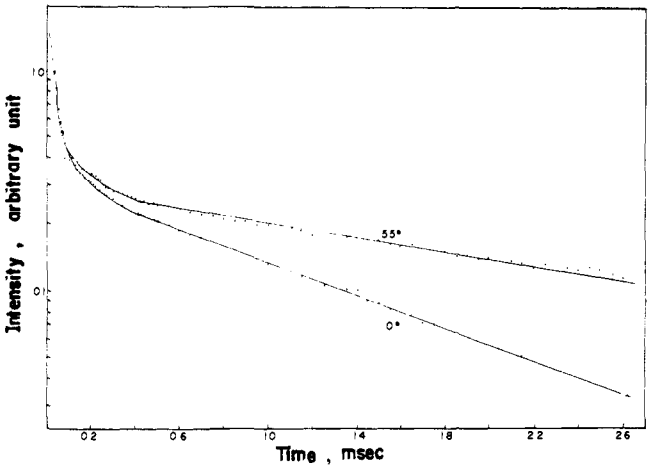

Figure 1. Proton FID for lecithin at 20 MHz and 25° at two different angles of orientation for a macroscopically ordered sample with ca. 74% lecithin in D_2O.

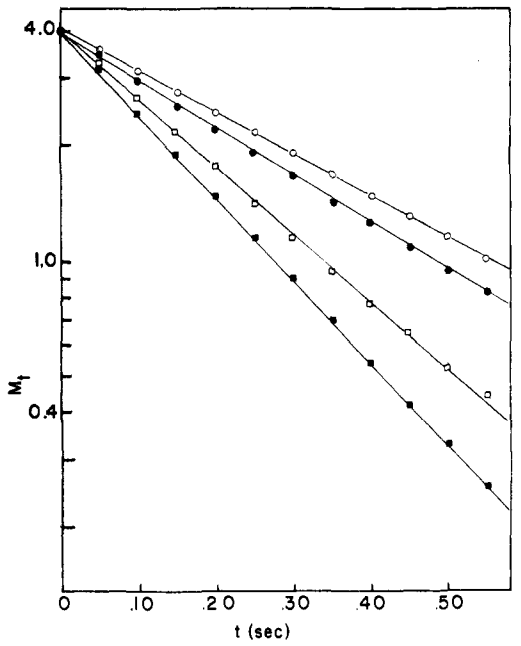

Figure 2. Plots of the superposition of two exponentials $M = A\exp(-t/T_{1A}) + B\exp(-t/T_{1B})$, with T_{1A} = 0.20 sec and T_{1B} = 0.40 sec: (○) $A = 4, B = 0$; (●) $A = 3, B = 1$; (□) $A = 1, B = 3$; (■) $A = 0, B = 4$.

protons and for the methyl groups in Table I infer that the spin-lattice relaxation time of the methylene protons cannot have any systematic dependence with respect to the orientation of the lecithin molecules in the magnetic field. Therefore, spin diffusion is unlikely to be the major relaxation mechanism for the methylene protons.[26]

A major argument that led to the previous postulation of the spin-diffusion mechanism is that, in the T_1 measurement, the recovery of the magnetization of all the protons for unsonicated lecithin in D_2O displays a singular exponential behavior,[14,17,18,20] and, therefore, there must be a single relaxation time for all protons. We submit that this is an invalid argument for the following reason. The sum of two or more exponential decays appears deceptively like a single exponential if the decay times and the weighting factors for each component are similar. Figure 2 shows such an example, in which straight lines are drawn through the single exponentials as well as the sum of two exponentials in semilogarithmic plots. In the empirical determination of T_1, because of experimental errors involved, it would be difficult to differentiate the sum of two or more exponentials with not very different T_1's. Furthermore, the data in Table I show that, in the lecithin bilayers, the methylene protons must have a shorter T_1 than the methyl protons.

The T_1 data listed in Table I were obtained by measuring the recovery of the magnetization of the FID after the 180°-τ-90° pulse sequence in the following way. The data for "all" protons were measured at 40 μsec after the 90° pulse because of the limitation of the "dead time" of the spectrometer; the data for the methyl protons were measured at 400 μsec or more after the 90° pulse, because the methylene protons have essentially no contribution to that part of the FID.

It has been shown by the delayed Fourier transform method that even the choline methyl protons and the terminal methyl protons of lecithin have slightly different T_1 values.[13] Because of reasons discussed above, T_1 values measured from the recovery of magnetization are necessarily composite values for the superimposed signals. In principle, one could determine T_1 of the methylene protons by subtracting the contribution of the methyl signal in the magnetization plot; however, because of the experimental uncertainties involved, we were not able to obtain satisfactory and reproducible results from such a mathematical treatment. Furthermore, although the signals for the choline methyls and the alkyl methyls can be separated by the delayed Fourier transform technique at high frequencies and temperatures,[13] it would not be feasible to do so at the lower frequencies and temperatures. Therefore, only the T_1 data for the composite methyl protons will be treated quantitatively. T_1 values of the methylene protons would give more information on the motions of the lecithin molecule; unfortunately, they cannot be determined separately for the reasons stated above.

Proton T_1 for the Methyl Groups

Proton T_1 values of the methyl groups for three lecithin-D_2O systems at five frequencies are presented in Figures 3-5 as a function of temperature. There are several prominent features in those figures. First, above 20°, where the systems are in the liquid crystalline lamellar phase, T_1 decreases slightly with the decrease of the D_2O-lecithin ratio. Second, the T_1 curves show obvious inflections at the liquid crystal to gel transition and at about −35°. The transition temperature for the lamellar phase to the gel phase is de-

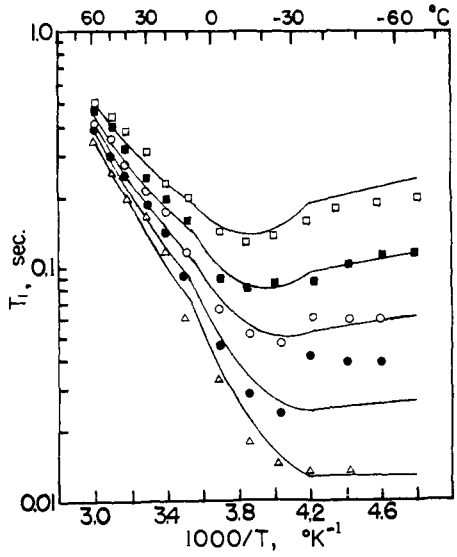

Figure 3. T_1 of methyl protons of lecithin for a sample with 58% lecithin in D_2O. The resonance frequencies were: □, 60.0; ■, 35.0; ○, 20.1; ●, 10.5; and △, 5.2 MHz. The solid lines represent calculated data.

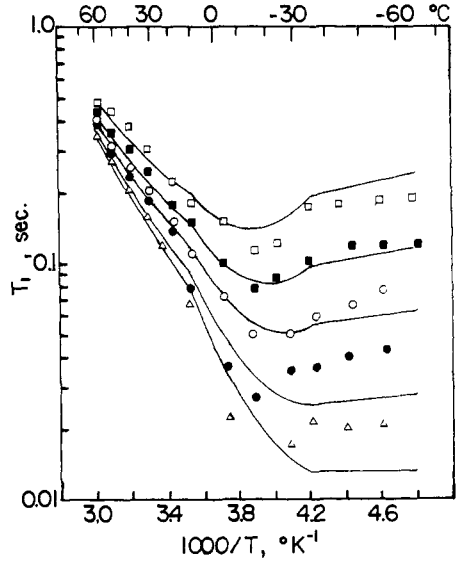

Figure 4. T_1 of methyl protons of lecithin for a sample with 67% lecithin in D_2O. The resonance frequencies were: □, 60.0; ■, 35.0; ○, 20.1; ●, 10.5; and △, 5.2 MHz. The solid lines represent calculated data.

pendent upon the concentration and ill-defined (accurate to ±3°),[1] because egg yolk lecithin is a mixture of lecithins with different fatty acyl chains. Using the phase diagram determined by Small,[1] and considering the difference in molecular weight between H_2O and D_2O, the transition temperatures for samples with 58, 67, and 74% lecithin were taken as 8, 10, and 12°, respectively, in the calculations (to be discussed below). Experimentally, the temperature for the inflection in T_1 is not well defined; however, there is no doubt that such an inflection exists, especially at lower frequencies (Figures 3-5). The inflection in T_1 at the phase transition was overlooked by most previous investigators either because T_1 was measured at a single and relatively high frequency[16] or due to unsatisfactory temperature control.[13] However, a recent paper reported a similar inflection in T_1 at 8.5 MHz.[21] The leveling of T_1 below ca. −35° was reported before for a single frequency.[15] The third interesting feature of these results is that, below the transition temperature, T_1 does not show a systematic dependence on the D_2O-lecithin ratio in the concentration range studied. Thus, the solid curves drawn below the transition temperature in Figures 3-5 were calculated from the same parameters for all three systems, whereas the curves drawn above the transition temperature were calculated using different activation energies (Table II). The method of calculation is discussed in the following.

In both the liquid crystalline and the gel phases, the methyl group should behave like an anisotropically reorienting rotor, and T_1 for each methyl group should, thus, be dependent upon the orientation of its axis with respect to the field. However, the observed T_1 is a composite of the T_1 values of the five methyl groups (three in the choline residue, and one each in the hydrocarbon chains). Since the

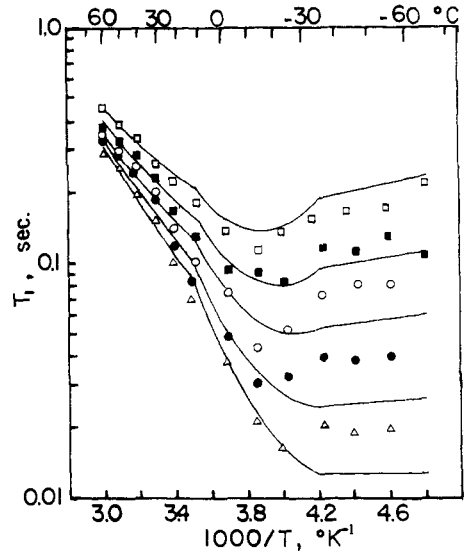

Figure 5. T_1 of methyl protons of lecithin for a sample with 74% lecithin in D_2O. The resonance frequencies were: □, 60.0; ■, 35.0; ○, 20.1; ●, 10.5; and △, 5.2 MHz. The solid lines represent calculated data.

axes of the five methyl groups form different angles with respect to the field and they undergo restricted motions, it is not surprising to find that the composite methyl T_1 does not show any discernible angular dependence in oriented lecithin samples (Table I). It should be emphasized that the situation of the methyl groups is different from that of the methylene groups: in the lecithin multilayers, the hydrocarbon chains are well oriented, and the directions from the

Table II. Parameters for the Calculation of Proton T_1 for the Methyl Groups in the Lecithin-D_2O System

	% lecithin	σ_0^2, rad^2 sec^{-2}	α_0, °K$^{-1/2}$	$\tau_{0\infty}$, sec[a]	E_a, kcal/mol
Crystalline and gel phases	58, 67, 74	3.36×10^9	2.53×10^{-2}	9.0×10^{-19}	11.0 (above −35°) 1.5 (below −35°)
Lamellar liquid crystalline phase	58	3.36×10^9	2.53×10^{-2}	4.6×10^{-15}	6.2
	67	3.36×10^9	2.53×10^{-2}	8.7×10^{-15}	5.8
	74	3.36×10^9	2.53×10^{-2}	2.3×10^{-14}	5.2

[a] The values of $\tau_{0\infty}$ for the liquid crystalline phase were chosen such that $\tau_0 = \tau_0 \exp(E_a/RT)$ was continuous at the phase transition point and was not a variable parameter.

methyl rotors to the methylene protons or from the methylene groups near the end of the chain to other methylene groups do not spread over a large angular range. Therefore, if the methyl groups and the terminal methylenes act as heat sinks, as postulated in the spin diffusion mechanism,[13,16] a regular dependence of the T_1 for the methylene groups on the orientation of the lecithin molecules in the magnetic field would be expected unless the methylene groups undergo considerable segmental motions.[26]

In order to interpret the composite methyl T_1 data, we treated the systems as having a distribution of correlation times. The actual distribution of the correlation times would be discontinuous and their contributions to $1/T_1$ would involve different weighting factors determined by the geometry and the segmental motion of different parts of the lecithin molecule. Such an exact solution would be extremely difficult and would involve too many undetermined parameters. In addition, it has been pointed out that the intermolecular relaxation may not be negligible in lecithin bilayers.[7] In order to avoid the difficulty of estimating the details of the motional behavior of the lecithin molecules and of separating the inter- and intramolecular contributions, we have employed the approximation of a continuous distribution of the correlation times in the form of a log-Gaussian Function:[27]

$$g(\tau) = \frac{\alpha}{\sqrt{\pi\tau}} \exp[-(\alpha \ln \tau/\tau_0)^2] \quad (1)$$

where τ_0 is the median of distribution and α is a parameter whose reciprocal determines the width of the distribution. Such a distribution function has been proved to be useful in describing the magnetic relaxation of many chemical and biological systems.[28-32] To account for the temperature dependence of T_1, it is further assumed that the median of the correlation time and the width parameter vary with temperature according to the relations:[29]

$$\tau_0 = \tau_{0\infty} \exp(E_a/RT) \quad (2)$$

and

$$\alpha = \alpha_0\sqrt{T} \quad (3)$$

respectively. The spin-lattice relaxation rate is then

$$\frac{1}{T_1} = \frac{2\sigma_0^2}{3}\left[\int_0^\infty \frac{\tau}{1+\omega^2\tau^2} g(\tau)d\tau + \int_0^\infty \frac{4\tau}{1+4\omega^2\tau^2} g(\tau)d\tau\right] \quad (4)$$

where

$$\sigma_0^2 = \frac{3}{5}\gamma^4\hbar^2 I(I+1)\sum_{j,k} r_{jk}^{-6} \quad (5)$$

and ω is the Larmor frequency. In eq 5, γ is the gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π, I is the nuclear spin number, and r_{jk} is the internuclear distance.

In the calculation, $\tau_{0\infty}$, E_a, α_0, and σ_0^2 are treated as variable parameters. This method of calculation has been discussed previously.[27,29] Values of those parameters that yielded the best fit with experimental data are listed in Table II, and the computed T_1 vs. $1/T$ curves are shown in Figures 3-5.

Interpretation of the Methyl T_1 Data

From the data presented in Figures 3-5 and Table II, it can be seen that for the gel and crystalline phases, T_1 of the methyl protons is independent of the concentration in the range studied. In other words, in these two phases the increase in the concentration of water does not significantly alter the motional behavior of the lecithin molecules. At higher frequencies, the T_1 values exhibit minima with respect to temperature because $\omega\tau_0$ is of the order of unity (actually at the minima $\omega\tau_0 \sim 0.7$ for the distribution function we used; for example, at $-23°$, $\tau_0 = 3.2 \times 10^{-9}$ sec from the data in Table II, and T_1 shows a minimum for ν = 35 MHz). It should be stressed that τ_0 is the median of the correlation time in the log-Gaussian distribution and should not be interpreted as the correlation time of the methyl rotation. Also, the "activation energy" (E_a) of 11.0 kcal/mol (eq 2, Table II) does not correspond to that of the methyl rotation, which should be much smaller for the lecithin molecule. It is a composite value for different motions for various parts of the molecule including intermolecular interactions and cannot be simply interpreted. This is to be compared with the results of Feigenson and Chan, who were able to resolve the signals for the two types of methyl groups at 220 and 100 MHz, and treated the T_1 data with the approach of a rotating top undergoing anisotropic reorientation.[13] The mean correlation time we obtained lies between the values of the two correlation times (about the rotor axis and off-axis excursions, respectively) they estimated, which is entirely reasonable.

An interesting feature of the methyl T_1 at lower temperatures (below about $-35°$) is that T_1 shows only a small temperature dependence for a given frequency. A similar observation for several synthetic lecithin-D_2O systems was reported but no explanation was offered.[16] This change in the temperature dependence of T_1 does not correspond to another phase transition, the freezing of some of the water molecules, which occurs at about 0°. It has been shown by differential thermal analysis[33] that approximately 8-10 water molecules per lecithin molecule are "nonfreezable" down to $-100°$, and no other phase transitions in that temperature range were reported. We suggest that the change in the temperature dependence for the methyl T_1 below ca. $-35°$ is due to the freezing of the segmental motions of the lecithin molecule; below that temperature the only important motion would be the rotation of the methyl groups, which would have very low activation energy (a value of 1.5 kcal/mol was used in the calculation), because none of the methyl groups is sterically hindered. This is compatible with the observation of an abrupt increase in the proton line width when the temperature was lowered below ca. $-40°$ for polycrystalline 1,2-distearoylphosphatidylcholine[34] and a minimum in $T_{1\rho}$ at $-23°$ for 1,2-dipalmitoyl-L-phosphatidylcholine monohydrate.[15]

From the point of view of treating lecithin bilayers as a model membrane system, the liquid crystalline phase at temperatures above ca. $+10°$ is of most interest. It can be seen from Figures 3-5 that the methyl T_1 does show an inflection at ca. 10°, and above that temperature T_1 at a given frequency is larger for a more dilute solution. This indicates that in the liquid crystalline phase the magnetic interaction of the methyl protons with other parts of the system is dependent upon the water concentration, in direct contrast to the situation in the gel phase. The change is not likely due to a change in the dipolar interaction between the methyl protons and the D_2O molecules, because the magnetic moment of the deuterium nucleus is small and the distances between the two kinds of nuclei are large. Thus, the increase in the water concentration in the liquid crystalline phase seems to bring about a corresponding change in the configuration of the lecithin molecule in the bilayers, causing the motion of the methyl groups to be less restricted, and/or to reduce the interactions between different chains in lecithin and between different lecithin molecules. This is in agreement with the findings of Small,[1] who determined that in the multilayer phase the addition of water not only thickens the water layer between the lecithin bilayers, but

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.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. GP-34202.

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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-