Effect of Structure and Charge on Radiation-Induced Reactions in Micellar Systems

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The process of detergency may be listed as one of the oldest physicochemical techniques used by man, and a strong and well-established chemical industry has grown over the years to support it. A detailed knowledge of detergency processes has been available for many years.[2] One aspect of detergents that is of prime importance is their ability in water to form aggregates called micelles. In recent years the pace of research in micellar chemistry has increased sharply, especially with the development of new spectroscopic techniques such as NMR,[3] ESR,[4] laser Raman,[5] and ultrasonic sound absorption.[6] This Account concerns itself with yet another new facet of micellar chemistry, the chemistry of radiation-induced reactions in these systems, and in particular the influence that micellar charge and structure play in these reactions. Earlier studies[7] have indicated pronounced and intriguing effects of radiation on colloidal and micellar systems.

There are several standard texts describing micelles and micellar phenomena.[2,8-10] Basically it can be stated that in aqueous solution surfactant molecules such as sodium dodecyl sulfate (NaLS) or cetyl trimethylammonium bromide ($CetMe_3NBr$) form aggregates called micelles. These are formed above a certain surfactant concentration known as the critical micelle concentration (cmc). These micelles may be roughly spherical, disklike, or rod shaped, depending on the conditions prevailing in the solution. The charged sulfate or ammonium head groups are directed toward the aqueous phase and the long hydrocarbon chains are directed away from the water, forming an oil-like core of the micelle. There is some evidence[11] that the micelle core also contains water, but no precise agreement is available on the issue at this time.[12]

The surface of the micelle is envisaged as containing charged head groups. For example, in NaLS micelles, about 20% of the sulfate groups are dissociated and charged, and about 80% neutralized by the counter sodium cations. A similar situation exists in other ionic micelles, and the net charge on the micelle can be changed (to some degree of accuracy) by addition of inert salts containing counterions of the micelle, e.g., Na_2SO_4 or NaBr, etc. The surface, or Stern layer, of the micelle has been investigated by probe molecules sensitive to the polarity of the environment.[13,14]

The micellar interior is viscous, as illustrated by the polarization of fluorescence of probe molecules dissolved in the micelle.[15,16] Microviscosities approaching 100 cP have been measured. In a similar fashion, laser Raman studies[5] are interpreted in terms of a partial ordering of the hydrocarbon chains into structures that lie intermediate between liquid and solid decane. Addition of solutes, i.e., salts which alter surface charge, and benzyl alcohol,[5,16] which binds to the surface, sharply affect the interior viscosity of micelles.

The preceding discussion illustrates that many structural features of micelles, both core and surface, are fairly well understood. In this Account we will discuss how certain conventional reactions that have been studied in homogeneous solution may be studied to advantage in micellar systems.[17-19] Reactions induced by low-energy photons (photochemistry) or high-energy photons or fast electrons (radiation chemistry) can be studied in micellar systems and the effect of micellar charge and structure on these reactions ascertained. Micelles provide a means of organizing the reactants on a molecular scale and thus enhancing or retarding reaction. Comparison of the micellar data with data from homogeneous solutions often leads to interesting molecular details of the reactions and also enables one to comment on micellar structure.

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Experimental Details

The solubility of arenes in water is low ($<\sim10^{-6}$ M),[20] but relatively high concentrations ($\sim10^{-2}$ M) may be achieved by using surfactants. Several studies, including pulse radiolysis and photolysis,[21] suggest that the arenes are solubilized by micelles. Photochemical excitation of the arene in the micelle leads to excited singlet and triplet states,[22] whose reactions may be monitored by fast spectroscopic techniques.[19] Ionic and free-radical reactions may also be initiated in those systems by radiolytic methods.[23] A comparison of the reaction in micellar and homogeneous solutions then comments on the influence of the micelle on these processes.

Location of the Probe Molecule in the Micelle. It was indicated earlier that many micelles may be envisaged as roughly spherical or oval structures with hydrocarbon-like cores and polar exteriors. A probe molecule may be adsorbed to the surface of the micelle or, alternatively, the probe may be solubilized in the hydrocarbon core. Several studies provide useful information on the location of the probe P in the micelle.

NMR. Several proton NMR studies[3,10,24] show that probes such as benzene and naphthalene have a hydrocarbon-like environment in micelles. These statements result from observations that the location of the proton NMR spectra of the probe in micelles is similar to that in hexane rather than that in water. This indicates that a molecule such as benzene is located inside the micelle and away from the polar environment of water.

Other studies[10,25] have utilized the chemical shift measurements of the proton NMR spectra of the micellar protons induced by the probe. For example, the presence of the probes pyrenesulfonic acid (PSA), pyrenebutyric acid (PBA), or pyrene (Py), in micelles of $CetMe_3NBr$, leads to chemical shifts of the *N*-methyl protons, the main-chain methylene protons, and the main-chain methylene and terminal methyl protons, respectively. These data indicate that the pyrene chromophore is located at the micelle surface with PSA, just within the micelle with PBA, and further inside with Py. An approximate location of the proteins is thus established.

Other studies make use of the effect of environment on the spectral properties of probe molecules. Pyrene itself shows a fluorescence with distinct vibrational structure (Figure 1). The vibrational bands may be numbered I–V. A detailed study[26] shows that the III/I band ratio varies with solvent polarity, and the ratio III/I of pyrene in micelles can be used to gain some measure of the polarity of the probe environment in these micelles. The environment of pyrene in $CetMe_3NBr$ is similar in polarity to pyrene in alcohol. The polarity decreases if the methyl groups of

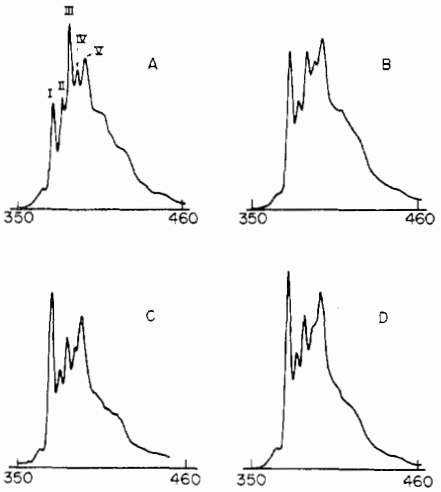

Figure 1. Fluorescence spectra of pyrene in solvents and micelles: (A) C_6H_{12}; (B) NaLS; (C) methanol; (D) $CetMe_3NBr$.

$CetMe_3NBr$ are replaced by H atoms, as with dodecylammonium chloride ($DodNH_3Cl$). Changing the polarity of the micellar surface by varying the ionic strength of the solution has no effect of the ratio III/I. This shows that pyrene is located away from the polar surface. It is suggested that the polar environment is provided by water penetration into the micelle. This is larger in $CetMe_3NBr$ than in $DodNH_3Cl$, due to the more bulky head group structure of $CetMe_3NBr$, which contains methyl groups. A more compact structure prevails with $DodNH_3Cl$, due to the smaller proton head groups. The penetration of water into the micelle is thus lowered, and a less polar environment then exists for pyrene.

A probe molecule such as pyrenecarboxaldehyde (PyCHO) is located in the head groups of micelles, and dramatic changes in the probe fluorescence characteristics are observed on changing the surface potential of the micelle by varying the ionic strength of the solution.[27]

The above data show that it is possible to approximately locate a selected probe molecule in a micelle. The probes normally used are large, e.g., pyrene, so it is not critical to define the precise location of the probe. The most probable location on the micelle surface, or inside the micelle, is all that is required. General experience indicates that molecules such as benzene or pyrene which do not possess hydrophilic groups tend to locate in the hydrocarbon part of the micelle, although H_2O penetration of the micelle may lead to a rather polar environment. Molecules such as aminopyrene, PSA, and PyCHO which possess hydrophilic groups tend to locate toward the surface of the micelle with the hydrophilic group in the Stern layer. These considerations are important when considering the nature of radiation-induced micellar reactions of probe molecules in micellar systems.

Reaction of Noncharged Species in Micelles. *Reaction of Excited States.* It was realized quite early that micellar systems catalyzed many reactions.[10,28] One of the simplest photochemical processes that is catalyzed by micellar systems is the formation of excimers of pyrene[7a,25b,29] from the interaction of excited

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pyrene and ground-state pyrene (eq 1). In solvents of

$$Py \xrightarrow{h\nu} Py^* \overset{Py}{\rightleftarrows} (Py)^*_2 \quad (1)$$

viscosity ~1 cP, significant yields of pyrene excimers are only formed at concentration of $>10^{-3}$ M. However, in micellar solutions, excimers are formed at concentration of 10^{-5} M. It has been established[25b,29] that the excimers are formed only on excitation of micelles containing two or more pyrene molecules; micelles containing single pyrene molecules exhibit only monomer fluorescence. The distribution of pyrene among the micelles follows a Poisson distribution, and the ratio of excimers to monomers can thus be calculated. The excimers are formed rapidly in times $<10^{-7}$ s as required by the locally high [Py] in micelles containing more than one pyrene molecule. The catalytic effect is entirely due to a local increase of the [Py] in micelles over that in the bulk of the solution.

The formation of rodlike structures from spherical micelles by addition of salt leads to an increase in the excimer yield.[25b] This is due to the formation of a few large rod micelles at the expense of the small spherical clusters. Hence, the condition where several pyrene molecules are localized within a small region of space, namely the rod micelle, becomes more pronounced. The rate of excimer formation still depends on the mobility of the pyrene molecules within the micelle. Estimates of the local microviscosity of spherical and rod-shaped micelles from such data are 25 and 80 cP, respectively. Surface probe studies show no increase in the viscosity experienced by a probe on the surface of a rod compared to spherical micelles. The data clearly indicate the role played by micellar size, shape, and viscosity on the movement of molecules in the micellar interior.

Pyrene fluorescence may also be efficiently quenched by a suitable molecule located within the micelle, e.g., iodoheptane, or a molecule located on the surface, e.g., I^- or Br^-. The latter effects will be discussed subsequently. The rate constant for quenching of excited pyrene by iodoheptane in methanol is 5×10^8 M^{-1} s^{-1}. This indicates a relatively low quenching efficiency, and iodoheptane concentrations of $\sim 10^{-2}$ M are required for efficient quenching. However, small concentrations ($\sim 10^{-4}$ M) of iodoheptane efficiently quench pyrene fluorescence in NaLS micelles. Greater than 95% of the iodoheptane is dissolved in the micellar phase in these systems. Analysis of the data shows that only micelles containing iodoheptane and excited pyrene lead to fluorescence quenching.

External Quenching of Pyrene Fluorescence. Various "quencher" molecules such as triethylamine, thallous ion, iodide ion, etc., quench pyrene fluorescence both in homogeneous and in micellar solutions.[16,21,30,31] These quenchers reside in the aqueous phase of the micellar system and cross into the micellar phase to react with excited states of pyrene. The quenching reaction mechanism requires that the quenching

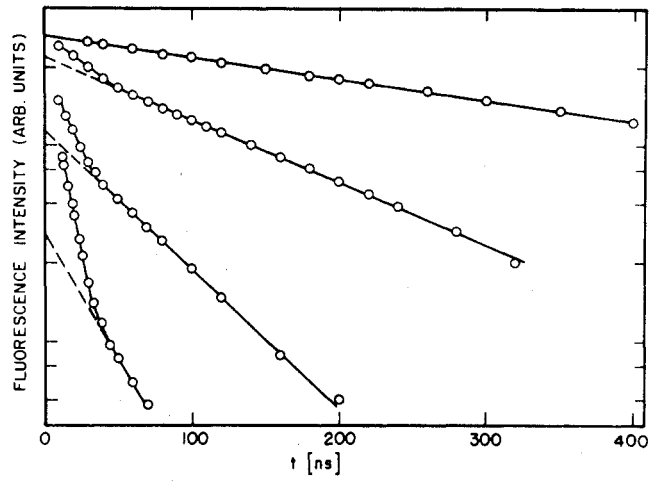

Figure 2. First-order decay curves of pyrene fluorescence vs. time in 0.1 M NaLS micelles at different CH_2I_2 concentrations. From the top downward: $[CH_2I_2] = 0$, 2.9×10^{-4} M, 5.8×10^{-4} M, and 1.6×10^{-3} M, respectively.

molecule enter the micelle rather than that the excited pyrene exit into the aqueous phase. Several facts favor this mechanism. (a) The exit time of pyrene and anthracene into the aqueous phase has a lifetime greater than 1 ms,[32] whereas the quenching rates occur in <100 ns. (b) The nonaqueous environment of pyrene (fluorescence, fine structure determination) does not change during the time period of the quenching reaction. (c) Certain quenchers, e.g., triethylamine, form an excited complex (exciplex) on quenching with excited pyrene. The properties of these complexes vary with environment. In a nonpolar environment the exciplex is stable and luminesces. In water and polar environments the exciplex dissociates to ions. In a micellar system a luminescent exciplex is observed on excitation of pyrene–triethylamine, showing that the environment of the two species on quenching is nonpolar.

In summary, the evidence strongly favors the interaction of the quencher molecule with excited pyrene in the micellar system rather than in the aqueous phase. Thus far, micellar quenching reactions of two strict types have been described, viz., the quenching (iodoheptane) residing in the micelle and the quenching by Tl^+, I^- which reside in the aqueous phase and penetrate into the micelle. A more general condition, which combines the two above interactions, is achieved with certain molecules such as diiodomethane, CH_2I_2.[32] Due to its solubility characteristics, this molecule may reside both in the micelle and in the aqueous phase. The kinetics of quenching of excited pyrene are thus complex. Figure 2 shows the pseudo-first-order plots for quenching of Py* by CH_2I_2.

In the absence of CH_2I_2 the decay of Py* is uniquely exponential over the time range studied. As $[CH_2I_2]$ increases the rate of decay of Py* increases, and two distinct processes are observed. The faster one, the extent of which increases with $[CH_2I_2]$, is due to the decay of Py* in micelles which already contain CH_2I_2. The slower decay, the extent of which decreases with increasing $[CH_2I_2]$, is due to a situation where CH_2I_2 enters the micelle from the aqueous phase in order to quench Py*. The total kinetics of the system are as

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follows: (a) distribution of CH_2I_2 between micelle and water; (b) rate of entry of CH_2I_2 into micelles; (c) rate of exit of CH_2I_2 from micelles; (d) rate of quenching of Py* by CH_2I_2 in micelles. All parameters can be determined from the data.[32]

This general condition is complicated and, in order to simplify quenching reactions for the study of micellar systems, a quencher is chosen which resides in the aqueous phase and which enters the micelle in order to quench Py*. Thus a comparison of the quenching rate of Py* by benzene in the micellar system to that in homogeneous solutions (alcohol, alkanes, etc.) reflects on the modification of the reaction by the micelle, viz., movement of Py* in the micelle and quencher into the micelle. Some examples are given below, and a list of quenching rates in various micelles is given in Table I.

Anionic Micelles. The quenching rates in anionic micellar systems of excited pyrene by various solutes are listed in Table I. The rates vary from micelle to micelle and tend to inversely follow the microviscosity of the micelle. For the most part the micellar rate constants are lower than those observed in homogeneous solutions. The data indicate an inhibition of movement of quencher to the pyrene. Brevity of space does not permit a detailed discussion of the reaction rates shown in Table I. However, the following experimental conditions markedly affect the reactions initiated in the micellar systems and comment on penetration of the micelle by the quencher molecule. (a) A structural change from a sphere to a rod increases the reaction rate. (b) Increased micelle rigidity by addition of Mg^{2+} decreases the reaction rate. (c) Decreased rigidity by adsorption of benzyl alcohol or cholesterol increases the reaction rate. (d) Repulsion of like-charged quenchers from the micelle surface decreases the reaction rate, and vice versa for oppositely charged species. Neutralization of the micelle charge by increased ionic strength decreases these effects.

An interesting situation arises if the quencher molecule is absorbed on the surface of the micelle. Quenching of Py* then occurs only if Py* reaches the surface of the micelle. This is noted with NaLS, and Tl^+ and $CetMe_3N^+(Cl^-, Br^-,$ and/or $I^-)$ micelles. The rate of quenching often reaches a plateau where the rate becomes independent of benzene concentration. This is interpreted as a situation of maximum adsorption of benzene to the micelle and the rate-limiting step is then the movement of Py* within the micelle to the surface.

Cationic Micelles. The above effect is quite pronounced for cationic micelles. Figure 3 gives data for the quenching of Py* in $CetMe_3NBr$ micelles. The lifetime of Py* in $CetMe_3NBr$ is 100 ns and significantly lower than that of Py* in NaLS or in $CetMe_3NCl$. This is due to the Br^- quenching of Py* at the micellar surface. Similar effects are noted for naphthalene[33b] and perylene[33c] in $CetMe_3NBr$ micelles. Addition of Cl^- replaces the bound Br^- and the lifetime increases since Cl^- does not quench Py*. The effect is similar but more pronounced for SO_4^{2-} ions, and less pronounced for OH^- ions. These data reflect the less efficient binding of OH^- to the micelle compared to both Cl^- and SO_4^{2-}. The addition of benzyl alcohol also increases Py*

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Table I
Rate Constants (10^9 M^{-1} s^{-1}) for Reactions in Micelles[a]

Reaction	Water or alcohol	NaLS	NaTC	NaTC/3% cholesterol	Sodium oleate	$CetMe_3NBr$	Brij 35	Igepal CO-630	Triton X-100	Bilayer distearyl-lecithin	Lyso-lecithin micelle
Py* + O_2	20.9	9.2	4.6	7.3	7.0	3.5 (4.3)[e]	2.4	5.5	5.7	2.7	7.2
Py* + CH_3NO_2	8.1	3.0	0.12			1.8	1.7	0.53	0.51	0.055	0.57
Py* + Cu^{2+}	20.0	$\tau < 5 \times 10^8$ s^{-1}				$<10^{-3}$ (4.2×10^{-2})	2.7				
Py* + I^-	3.0	2.6×10^{-3} (1.9×10^{-2})	3.6×10^{-2} (0.38)[c] (2.2×10^{-2})[b] (7.3×10^{-2})[d]	5.4×10^{-2}	8.2×10^{-2} [NaCl = 0] 0.23 [NaCl = 0.15]	$\tau < 10^{-8}$ s	0.54	0.40	0.69	$<10^{-2}$	0.51
Py* + triethyl-amine	0.3	0.25 0.04[b] 0.40[c]	1.4×10^{-2} (0.16)[c]	4.2×10^{-2}	0.13						
Py* + Tl^+	5.0		$\tau < 6 \times 10^{-8}$			3.1×10^{-2}		0.16	0.22	$<10^{-3}$	0.39
e_{aq}^- + micelle		$<10^{-4}$	0.13			$<10^{-3}$		1.7×10^{-2}	3.8×10^{-2}		
e_{aq}^- + Py	10.0	$<10^{-2}$				$>10^2$		1.7	2.0	$<10^{-2}$	3.8
e_{aq}^- + biphenyl	5.0	0.13						3.8	4.0		
e_{aq}^- + PCHO	16.0	2.5								0.005	
e_{aq}^- + $PyNH_2$	14.0	1.1									

[a] Taken from ref 16, 21, 25, 30, 32, 33, 36, and 40. [b] 4×10^{-2} M $MgCl_2$. [c] 0.2 M benzyl alcohol. [d] 0.1 M NaCl. [e] Rod-shaped micelle. [f] Limiting lifetime of reaction at high [solute].

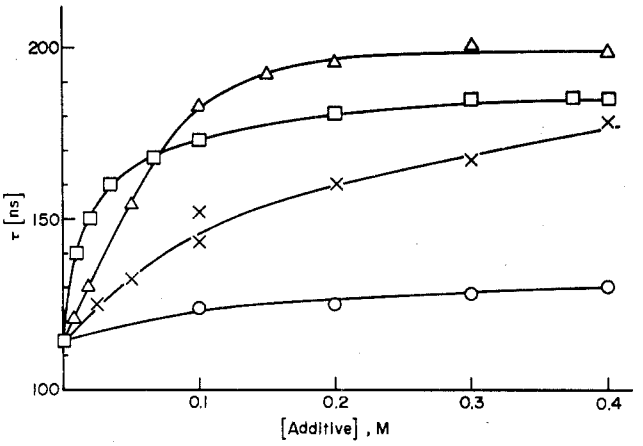

Figure 3. Effect of various additives on the fluorescence decay time of pyrene solubilized in 10^{-2} M $CetMe_3NBr$.

lifetime. This is due to the binding of benzyl alcohol to the micelle surface with a concomitant release of Br^- ions. This in turn decreases the efficiency of Py* quenching. Iodide ion quenches Py* very efficiently and to a much larger extent than Br^- ions. This is due to the larger size and hydrophobic nature of I^- ions. It is suggested that it penetrates further into the micelle than Br^- and leads to more efficient quenching.[34]

Reaction of e_{aq}^-. The advent of the hydrated electron, e_{aq}^-, into kinetics in the late fifties provided the kineticist with a means of studying reactions of the simplest anion in water.[17] Pulse radiolysis of water is a convenient method of producing this species. Significant quantities $\sim 10^{-5}$ M can be produced by intense bursts of high-energy radiation in liquid systems. The subsequent kinetics of e_{aq}^- can then be monitored by its strong absorption in the red part of the spectrum with spectral maximum at 720 nm. The physicochemical properties of these species are well reviewed in ref 17. The hydrated electron, e_{aq}^-, also has become a species of great interest in micellar chemistry, due to the important role that micelles play in photoionization in liquid systems. One of the products of photoionization is e_{aq}^-; hence independent studies of these species are important.

Micellar systems containing an added probe such as pyrene or with reactive centers such as cetylpyrridinium chloride or sodium taurocholate are pulse irradiated and the kinetics of e_{aq}^- monitored as reaction proceeds with the probe or reactive center in the micelle. Table I lists some reaction rates of e_{aq}^- with reactive entities in several micellar systems.

It is pertinent to study anionic micelles. These micelles should repel e_{aq}^- and subsequent reactions should be slow compared to homogeneous solution. This is observed for pyrene in NaLS where the rate constant is decreased over a hundredfold in the micelle solution. Neutralization of the micellar charge with added salt increases the rate of reaction as the repulsion of e_{aq}^- is decreased.[34b,c] Similar effects are noted for I^- quenching of pyrene in micelles.[30] Certain derivatives of pyrene, e.g., 1-aminopyrene and pyrenecarboxaldehyde, which are located at the micellar surface, react more rapidly than pyrene, the rate again increasing with decreasing micellar charge. There is some speculation on the mechanism of the reaction. It has been suggested that the electron tunnels from the aqueous phase to the reactive probe site in the micelle.[34c,35] However, it may not be necessary to invoke such a mechanism since it is known that H_2O penetrates micelles up to about four carbon atoms.[11,12] These channels of H_2O will provide a mode of transport for e_{aq}^- into the micelle to the vicinity of the probe. Alternatively some micelles may solubilize the probe close to the surface. It is expected that this will facilitate reaction with e_{aq}^-. The effect of micellar charge is mainly one of electrostatic repulsion of e_{aq}^- much after the fashion of similar charge effects with I^-.

An interesting situation occurs with $CetMe_3NBr$ micelles as the large positive charge of these micelles attracts the electron to the micelle. Reaction of the electron with micelle does not occur. However, a solute such as pyrene that is solubilized in the micelle reacts rapidly with e_{aq}^-, giving the anion. The attractive force of the micelle for e_{aq}^- catalyzes the reaction, and rate constants of 10^{11} to 10^{12} M^{-1} s^{-1} may be observed compared to 10^{10} M^{-1} s^{-1} in homogeneous solution.[36,37] Decreasing the micellar charge decreases the reaction rate. In some instances micelles promote electron-transfer reactions (viz., $CO_2^- + Py \rightarrow CO_2 + Py^-$ [36]) even though reaction does not take place in homogeneous solution. Both micellar catalysis (cationic micelles), and retardation (anionic micelles) effects on reactions of negatively charged species, e.g., e_{aq}^-, I^-, CO_2^-, etc., are explained in terms of the electrostatic nature of interaction of the species with the micelle. The nature of the motion of e_{aq}^- or I^- into the micelle to react with the probe, if this occurs, is a matter for debate. Fine details of micelle structure and probe location are needed to elucidate further some of these problems.

The rates of reaction of e_{aq}^- and I^- with probes in nonionic micelles, i.e., igepal or lysolecithin, are slower than in homogeneous solution.[38,39] The retardation effect may be ascribed to the reluctance of e_{aq}^- or I^- to leave the aqueous phase and enter the less polar region of the probe. These effects are not large for igepal and lysolecithin and rates are ca. one-tenth of those in homogeneous solution. They are similar to rates observed with surface probes in NaLS. The reaction rates of I^- and e_{aq}^- with pyrene in lecithin bilayers are, however, very slow, $<10^{-8}$ M^{-1} s^{-1}.[40] This is ascribed to the large separation of e_{aq}^- and I^- in the water phase from pyrene in the lipid. The phosphocholine head groups in these systems are much larger than in micelles. The probe is located near the fatty acid chains and separated from the aqueous phase by the head group. Since e_{aq}^- or I^- do not readily penetrate these lipid regions, reaction with the probe is retarded. Similar data are obtained with probes such as 1-aminopyrene and pyrenecarboxaldehyde which are

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located in the polar/nonpolar region. However, with these probes, if the large phosphocholine head group is removed, as, for example with phosphotydic acid, then reaction of e_{aq}^- with the probe proceeds with $k \sim 10^9\ M^{-1}\ s^{-1}$, a rate similar to that in NaLS. These last data reflect on the important role played by separation of e_{aq}^- and the probe in the two phases.

Photoionization. The efficiency of photoionization of aromatic solutes is greatly increased in micellar systems compared to other solvents. This is well illustrated by the two photon photoionization of pyrene which shows a large increase from solution in alkanes[41b] and alcohols[41a] and is most efficient in micellar solution.[41c] Photoionization in the latter solution leads to the cation in the micelle and the hydrated electron in the aqueous phase. The increasing yield of photoionization is a consequence of the increased probability of escape of the ion pairs with increasing solvent polarity.[42] Increasing the micelle size also leads to a decrease in the yield of photoionization due to the failure of the electron to escape from the larger micelles.[41c] In bilayers such as lecithin the large phosphocholine head group greatly reduced the escape of e^- to the aqueous phase. This is mirrored by the difficulty experienced by e_{aq}^- in returning from the water phase to the probe site.

In many instances the photoionized electron has an excess energy of ~1 eV, and may react with solutes solubilized at the micellar surface prior to solvation in the aqueous phase. This is reminiscent of the reactions of dry electrons observed in other systems.[43] The photoionization data indicate that the electron is thermalized ~18 Å for the micelle surface. This is in agreement with other data[44] that show that the range of a 1-eV electron is 10–100 Å in water.

Threshold for Photoionization. The threshold for photoionization is also greatly reduced in micellar systems compared to the gas phase or alkane liquids. The ionization potential in solution, I_s, will be reduced from that in the gas phase, I_g, by the polarization energy of the cation, P^+, and the energy of the electron in the solution, V_0: $I_s = I_g + P^+ + V_0$. Conservative estimates indicate that I_s could be 2–3 eV lower than I_g. Some initial measurements on these effects for phenothiazine in NaLS micelles, and in hydrocarbons, show that I_s in hydrocarbons is 4.5 eV, and 3.0 eV in NaLS micelles. These values are all considerably smaller than $I_g \simeq 6.5$ eV, but agree with the previous prediction. Several studies on enhanced photoionization in aggregated systems are now coming to light.[45]

Micellar systems are relatively well understood and may serve as very simple models for more complicated aggregated biosystems such as proteins and membranes. Indeed, the present micellar work has acted as a springboard for studies in both bile acid micelles,[33] globular proteins,[46] and lipid bilayers,[47] in bacterial membranes,[48,49] in differentiation of membranes of normal and virally transformed mammalian cells,[50] in nerve membranes,[51] and in blood-clotting processes.[52] New details of radiation-induced processes worked out in micellar systems often can be carried over profitably to more extensive biosystems. Micelles provide a unique opportunity for photochemists and radiation chemists to study the radiation-induced actions of species that are located fairly precisely and close to each other. It is possible that the molecular details of energy and electron-transfer processes can be studied in such systems. It is not beyond the imagination that the photo- and radiolytic processes may contribute details of micellar structure, surface properties, and kinetics of use to colloid chemists.

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