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Radiation-Induced Reactions in Organized Assemblies

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Contents

J. Kerry Thomas was born in Llanelli, Wales, and attended Manchester University as a State Scholar. He received his B.Sc. with honors in chemistry in 1954, and his Ph.D., in 1957, working with Professor J. H. Baxendale on the radiolysis of aqueous systems. After a year at the National Research Council, Ottawa, as a Postdoctoral Fellow, he served as a scientific officer at the British Atomic Energy Research Establishment from 1958 to 1960. In 1960, he joined Argonne National Laboratory, and studied free-radical mechanisms with Dr. Hugo Fricke and Dr. E. J. Hart. With Dr. J. W. Hunt he pioneered nanosecond pulse radiolysis studies, and for this work, he was awarded the honorary degree of Doctor of Science at Manchester University in 1969, and the research award of the Radiation Research Society in 1974. He moved to the University of Notre Dame in 1970 as a Professor of Chemistry, where he initiated photochemical research in micelles and other organized assemblies of importance in solar energy research. Dr. Thomas has been a guest professor at the Hahn-Meitner Institute in Berlin several times in the past 10 years.

I. Introduction

The interaction of radiation with matter and the chemistry ensuing from such processes are topics of continued interest to the scientific community in general. Vision, photosynthesis, certain types of pollution, and more recently energy storage are all examples of the important issues raised by the action of low-energy radiation with matter or the study of photochemistry. The photochemistry of both large and small molecules has received detailed attention by many different techniques ranging from chemical analysis of end products to direct identification of short-lived intermediates in the initial picoseconds (ps) of the photochemical process. It is evident that the intricacies of many photochemical systems are understood and that a further step in development could be via preferential control of certain aspects of a process. A clue to a possible approach is seen in the catalytic effects of various entities on thermal reaction. In particular, the effects of micellar systems on the rates of several organic reactions have been studied in some detail over the last 10 years,[1-6] stemming from the early observation of micellar catalysis of the reaction of crystal violet with phenol blue.[1]

Quite large enhancements of reaction rate have been observed in micellar systems and have been explained by two processes: (a) The micelle solubilizes both reactants in the same micellar volume, thereby increasing their local concentrations, and hence increasing the reaction rate. (b) The micelle–water interface can exhibit unique properties which influence a reaction. For example, the local electric field at the surface of ionic micelles can be as large as 10^6 V/cm.[7] Such a field could influence the transition state of a reaction and lead to an increased rate of reaction.

It is sufficient to say that micellar catalysis of thermal reactions is a well-established area of research which has provided new vehicles for catalysis studies. The prime object of this review is to wed together two well-established areas of research into a discussion of the effects of aggregated or organized assemblies, and in particular micellar systems, on photochemical reactions. The interest in this area of research is immediate as the organized assemblies may be looked upon as models for photoprocesses in biology and also as systems for storage of solar energy.[8–10] The concept in general is to utilize an organized molecular assembly to influence and direct a photochemical system incorporated in or near the assembly.

Further discussion of these types of experiments requires some explanation of, as well as pictorial representation of, the organized assemblies themselves.

II. The Nature of Organized Assemblies

In this review the term "organized" is applied broadly to any situation where some part of the system aggregates or organizes itself in deference to the bulk of the system, which could be a molecular liquid or solvent. The degree of organization can vary quite markedly from one type of system to another. For the most part, interest will center around colloidal systems in simple molecular solvents, such as water or hydrocarbons.

A. Alcohol Clusters

In hydrophobic solvents, alcohols cluster together to form a variety of nondiscrete aggregates.[11] These structures arise from hydrogen bonding between the alcohol OH groups. Little chemistry has been carried out in these systems; however, it is reported that electrons produced in these systems, via high-energy radiation,[12–15] are efficiently captured by the alcohol clusters and that absorption spectra typical of solvated electrons are observed. The spectra show an increasing blue shift with increasing alcohol concentration, which shows an increasing energy of electron solvation as the alcohol cluster increases in size. Similar data have been observed in the photoionization of various arene molecules in these systems when the photoejected electron is captured by the alcohol cluster.[16] Pulsed conductivity experiments show that the mobilities of the electrons differ in the various clusters, being larger in the small alcohol clusters at lower solvation energies.

The photochemistry of tetranitromethane in alkanes shows a sharp change on introduction of alcohol clusters.[17] In the presence of clusters the excited state of $C(NO_2)_4$ extracts an electron from the alcohol cluster, forming the nitroform anion:

$$C(NO_2)^*_4 + (\text{cluster}) \rightarrow C(NO_2)_3^- + (\text{cluster})^+ \qquad (1)$$

This process does not occur in alkanes. However, if alcohol clusters are introduced into the alkane, then solvation of the product ions by the clusters provides additional energy for the reaction and ions are observed.

The main feature of interest in these systems is the promotion of ionic reactions by additional solvation energy made available by the alcohol clusters.

B. Micellar Systems

Micelles are aggregated structures formed by the interaction of several surfactant molecules. Surfactant molecules are characterized by possessing both hydrophobic and hydrophilic moeities, and are often called amphiphiles. Usually the hydrophobic part is a long-chain hydrocarbon (eight C atoms or more), while the hydrophilic portion of the molecule may be a group of ethylene oxide units, as in the Triton series of surfactants, an anionic group, as in sodium lauryl sulfate, NaLS, or a cationic group, as in cetyltrimethylammonium bromide, CTAB. Above a certain concentration called the critical micelle concentration or cmc, the surfactant molecules group together forming micelles. A pictorial representation of a micelle is shown in Figure 1, where the hydrophobic groups form a core of the micelle separated from the bulk solvent, which is water, by the hydrophilic head groups. It is more or less agreed that micelles are distorted spheres or disks of small dimensions, 15–30-Å radius.[18–20] However, under certain conditions much larger micelles may be formed which are rodlike in character. To date little chemistry has been carried out in these latter systems, and they will only be mentioned in passing. Other physical properties of micelles, such as cmc, degree of aggregation, and ionic dissociation, have been recorded.[21,22]

A micelle is a dynamic structure which exists in equilibrium with its monomer, where monomer units are both leaving and entering the micelle.[23] The structures formed are fairly discrete, and the aggregation number of a micelle, which may be as large as 200 monomer units, is maintained over a range of experimental conditions. The core of the micelle is hydrocarbon-like and fluid, microviscosities of 10 to 30 cP having been measured by fluorescence polarization experiments.[24,25] In addition to these measurements, laser Raman studies show that the hydrocarbon chains exhibit a higher degree of order than bulk alkane of the same carbon number.[26]

In the case of ionic micelles a significant percentage (~20%) of the head groups are ionized, the counterions Na^+ or Br^- being in the region of the micelle surface or further into the aqueous bulk in the Stern layer. These ions are also in dynamic equilibrium with ions absorbed at the micelle surface.

There is much speculation on the degree of penetration of water into a micelle.[27] A penetration of two to four carbon atoms from the head group or surface is often quoted, although suggestions of penetration into the core have been made. It is difficult to reconcile this latter view with the thermodynamic picture of a micelle, where the driving force forming micelles is entropic and involves expulsion of water molecules from the vicinity of the alkane chains. In the present review, the former picture of limited water penetration is adhered to.

It is difficult to pin down the structures of micelles, which tend to differ quite significantly with the type of surfactant used. Another problem lies in the difficulty of making direct structural observations on micelles. Most of the statements on micellar structure are inferred from thermodynamic properties, or kinetic features of micelles. The representation in Figure 1 shows a rather disorganized array of surfactant molecules, which, however, show more order and distinctly different properties to solutions of the monomer surfactants themselves.

C. Reversed Micelles

Certain surfactants also form micelles in bulk hydrophobic solvents, such as heptane and benzene. Typical examples are sodium diisooctyl sulfosuccinate, or AOT, that forms reversed micelles in many solvents, benzylcetyldimethylammonium chloride, BDC, a cationic surfactant that forms reversed micelles in benzene, and dodecylammonium propionate, DAP, a nonionic surfactant that forms reversed micelles in benzene and hexane. These micelles have polar cores that may accommodate large amounts of water (Figure 1)[28] and a hydrophobic bulk phase. These systems are not as common as normal micelles, although AOT is used extensively industrially and its properties are well established. The radii of AOT micelles in heptane can vary from

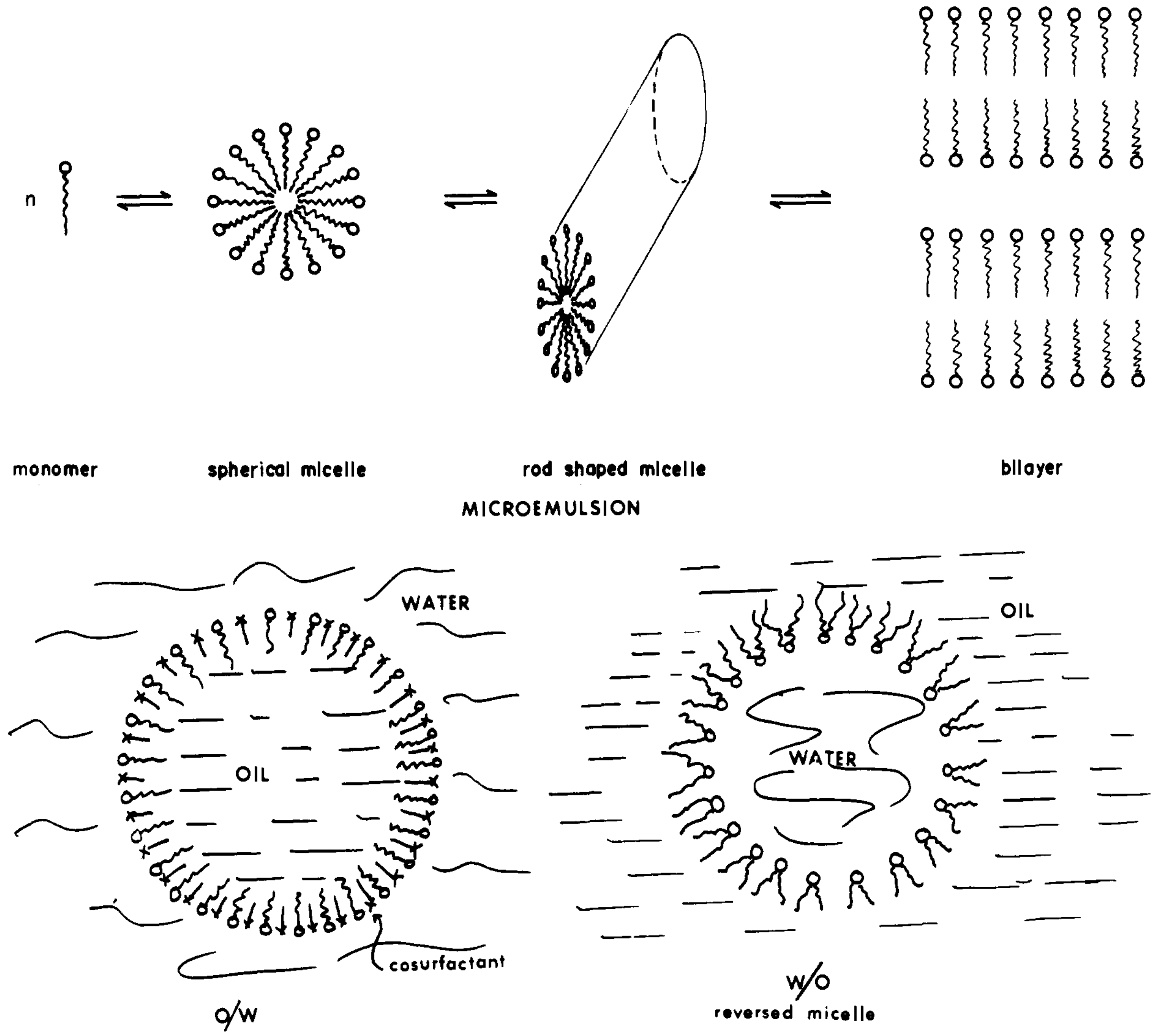

Figure 1. Aggregated structures: spherical micelle; cylindrical micelle; bilayer; microemulsion O/W, oil in water; microemulsion W/O or water in oil; reversed micelle.

15 to 80 Å, depending on the percentage of water in the system.[29,30] The nature of the water in the micelle core or pool has been investigated by fluorescence spectroscopy,[20] absorption and polarization spectroscopy,[29] and NMR studies.[30] It is found that the properties of bulk water are only approached at high water content, when H_2O/Na^+ ratios exceed 6. These properties have interesting effects on thermal[28] and photoinduced reactions[29,31,32] and will be discussed subsequently.

Reversed micelle systems containing water, unlike normal or regular micellar systems, possess three components, oil, water, and surfactant, as distinct from surfactant and water only. They may be looked upon as microemulsions.

D. Microemulsion Systems

A thick homogeneous cream is produced if an oil and water mixture is shaken vigorously with a surfactant. This solution is opaque to light, and not of use in photochemical studies. The introduction of a cosurfactant such as a long-chain alcohol, e.g., hexanol, into the system produces, if the conditions are correct, a clear solution of oil and water. The clarity of the solution is due to a breaking up of the large, opaque solution particles into smaller (~100 Å) spherical particles, which give rise to clear solutions which, however, scatter light. Many different systems of varying composition are known over the complete composition range of oil to water.[33-36] The clear solutions of oil in water consist of small colloidal aggregates (~100 Å radius) of oil, surfactant, and cosurfactant, and have been called microemulsions. A typical representation of an oil in water microemulsion is given in Figure 1. The particles are assumed to be roughly spherical, with a liquid oil core surrounded by a surfactant–cosurfactant interface with the aqueous bulk. These are oil-in-water microemulsions. The analogous water-in-oil microemulsions also exist. They contain aqueous cores and are similar to reversed micelles. Microemulsions, like micelles, catalyze many thermal reactions.

A distinguishing feature of a microemulsion is the larger dimension of the particle, which enhances solubilization of hydrophobic molecules. For example, a molecule such as chlorophyll has dimensions that approach those of many micelles. Solubilization is difficult in micellar solution, and could disrupt the normal micelle structure. The larger microemulsion provides adequate space for solubilization of large molecules and also provides more versatility in spacing of reactants. The use of a microemulsion is also less restricted than that of a micelle, and it is easier to locate solutes in the particle interior than in micelles. All classes of surfactant, cationic, anionic, and nonionic, form microemulsions, and the surfaces of these colloids are not unlike those of the corresponding micelles.

Further organization of surfactant systems can lead to the formation of liquid crystals[37] and vesicles.[38-41] The former, although of great industrial utility, have not attracted any significant photochemical studies. However, vesicles, because of their similarity to biological membranes, have received a great deal of study, in particular by photophysical techniques.

E. Vesicles

Figure 1 also illustrates a vesicle structure, which is a closed bilayer structure formed by lipids[38-41] or double chain surfactants.[42-45] The structure encloses a region of the solvent which is usually water, and may have a radius of 100 Å or greater. Vesicles may be envisioned as two concentric spheres of amphiphiles whose lipid sections are in contact, and separated from the inner and outer water phases by the polar head groups. Molecules may be trapped in the aqueous vesicle interior for significant periods of time (several days or weeks). Until recently vesicles were formed exclusively from lecithin structures; however, there are now several reports of synthetic surfactants which also form vesicles and which possess many of the properties of the standard lipid structures.

Apparently, the important feature of design for a surfactant vesicle is that the surfactant contain two long hydrocarbon chains rather than the one of micelle-forming surfactants. For example, dioctadecyldimethylammonium bromide forms vesicles, while octadecyltrimethylammonium bromide forms micelles. The double chain leads to geometric restrictions which favor vesicle rather than micelle formation.[46] A reduction in surface change is also required, i.e., a smaller degree of dissociation of head groups in order that the head groups can pack more closely together.

The unique photochemical feature of vesicles lies in the possibility of initiating reactions in the vesicle interior, followed by transportation of a product through the lipid bilayer to the aqueous bulk where further chemistry can take place. It is thus possible to compartmentalize the reaction system with beneficial results.

It now remains to briefly discuss aqueous inorganic colloids which act in an analogous fashion to the proceeding organic structures.

F. Clay Minerals

Bentonite clays in suspension in water form negatively charged colloids, presumably due to dissociation of Na^+ ions associated with SiO^- groups on the particle. Although these particles may be as large as 1 μm, nevertheless reasonably clear aqueous suspensions can be formed. A number of organic molecules as well as inorganic ions are absorbed on the clay particles.[47] Little photochemistry has been carried out in these systems; however, it should be possible to carry over much of the chemistry and systems studied in micelles to the clays. The inorganic nature of clay colloids could also introduce new and interesting features in photochemical studies as these structures are static and more organized than the organic structures described earlier.

G. Metal Clusters

Small metallic clusters of silver or gold are stabilized in aqueous solution by surfactant-like molecules, and it is reported that the redox chemistry of these systems is different from that of bulk metal. Although the means of constructing these systems has existed from the earliest days of colloid chemistry, it is only recently that their unique chemical properties have begun to be exploited. Colloidal platinum has been used to promote formation of molecular products from reactive free radicals,[50,51] an aspect which is important in the storage of solar energy.

There are numerous colloidal assemblies in nature and in the laboratory, a few of which have been indicated above. Some of the systems have already been shown to exhibit catalytic effects on photoinduced reaction, while others, due to their similarity to these systems, or due to catalytic activity in thermal reactions, are suggested as new areas of study for photochemists.

The reactions are carried out on or in colloidal assemblies, and a question of prime importance is the location of the reactants and reactant environment. In particular micelles and microemulsions will be considered, as most work has been carried out in these systems.

H. Spatial Location of Solutes

Previous sections have emphasized the dynamic nature of micelle (and probably microemulsion) systems, where rapid exchange of counterions and surfactant takes place between micelle and bulk phase. Material solubilized by these systems also undergoes similar kinetic patterns, and a solute must exist in dynamic equilibrium with the bulk and micellar phase. For significant solubilization by the micellar phase, the solute, on the average, spends most of its time with the micelle; residence times approaching milliseconds have been reported. Vesicles and clay colloids do not exhibit this type of dynamic equilibrium with a monomer phase; however, a solute associated with these structures may also exhibit dynamics of the kind described above. There is a report of a residence time of 1 s for pyrene in lecithin vesicles.[52] In clay systems, counterions such as Na^+ exhibit rapid kinetic reaction between the clay and the bulk phase.

One approach in micellar catalysis is to replace the counterion with an ion which is chosen as one of the reactants. Depending on the condition of the system, the reactant ion may be mainly bound to the micelle surface, be mainly confined to a region close to the surface, or exist in the bulk phase. A neutral solute could be solubilized in the micelle interior close to the surface, "in" the surface, or "on" the surface. These three positions are less well defined if the suggestion of micelle motion is considered.[53] Here it is suggested that the monomer units oscillate rapidly back and forth in the micelle surface leading to considerable deformity of the surface. A solute in the vicinity of the surface will thus experience a rapidly changing environment which sometimes places it within the surface and at other times on the surface. This fluctuation is considered to be rapid, and an average position or environment can be stated during a reaction period.

A further problem lies in the fact that many solutes have dimensions that are comparable to those of micelles, and a precise location is impossible. In the present review two solute positions will be used: (I) within the micelle and close to the surface and (II) on the surface and in close proximity to the aqueous bulk.

I. Alkanes

Simple alkanes, e.g., hexane, due to their similarity to the surfactant chains, are expected to solubilize in the micellar core. It was found that the solubilities of several alkanes in micelles were a little less than those found in typical hydrocarbon solvents.[54] This was explained in terms of a compression of the micellar core by the interfacial tension at the surface. The Laplace pressure of the micelle was calculated from the radius of curvature of the particle and used to correlate the micelle and free solvent solubilities. Good agreement of calculated and experimental solubilities in micelles was obtained, suggesting an internal solubilization of alkanes in micelles.

Aromatic molecules are suggested to be solubilized on, or at, the surface of small micelles.[55-58] These suggestions stem from spectroscopic and thermodynamic measurements. Proton NMR studies[58] indicate that different derivatives of an arene, e.g., pyrene (py), pyrenesulfonic acid, PSA, and pyrenebutyric acid, PBA, are located in different positions in CTAB micelles. Pyrene causes a large chemical shift of the surfactant methylene protons, while PSA mainly affects the N-CH_3 protons; intermediate effects are noted for PBA. The data suggest that pyrene is within the micelle and close to the surface, while PSA and PBA are predominantly at the surface. Fluorescence spectroscopy shows that other polar derivatives of pyrene, such as pyrenecarboxaldehyde, PCHO,[59] and aminopyrene, PNH_2, are also located at the micelle surface.

Swelling a micelle by addition of a cosurfactant, e.g., hexanol, or formation of a microemulsion leads to larger structures with more fluid cores; many probe molecules then penetrate further into these entities and away from the aqueous phase.[60]

The very nature of micelles leads one to question the environment of a molecule solubilized in these systems, and several techniques have been developed to throw light on this problem.

III. *Environment of a Molecule in Micelles*

Some properties of the alkane cores of micelles, vesicles, and microemulsions were indicated earlier, namely:

(a) Raman spectroscopy,[62–89] measuring the degree of alkane chain order in packing the core

(b) Fluorescence polarization,[70] measuring the fluidity of the probe environment (probably surface in micelles)

(c) Positronium annihilation, measuring the hydrophobicity of the probe location[71a]

(d) Sound velocity measurements, monitoring the movement of surfactant units[71b]

(e) Excimer formation,[72–78] measuring the ease of movement of probe molecules in the structure

The basis of the Raman work lies in the observation of intense bands at 1064 and 1124 cm^{-1} due to C–C symmetric stretching in an all-trans structure and also a band at 1084 cm^{-1} which is indicative of gauche isomers. These bands are indicators of the degree of ordering of the hydrocarbon chains in the aggregated structure and have been used to observe phase changes in vesicles and the rod–sphere transitions in cationic micelles. Raman spectroscopy also gives information on the nature of the ethylene oxide residues in nonionic Triton-type micelles. With long-chain ethylene oxide chains such as Igepal Co-880 and Brij 35, dihedral helical structures are formed, while with short ethylene oxide chains such as in Triton X100 and Igepal 630, a major portion of the ethylene oxide chains is in open coils. The laser Raman data have provided a useful picture of certain structural features of micelles, namely, that the alkanelike core has more order than an alkane liquid, and also information on the mantle structure of neutral micelles.

The degree of ordering of the alkane chains or micellar rigidity can also be studied by means of fluorescence polarization.[70]

A. Fluorescence Polarization

This technique was originated by Weber[70] following earlier suggestions by Perrin and is used extensively in biochemistry to study motion in membranes and proteins. A probe molecule, e.g., methylanthracene, is located in the structure of interest and excited by polarized light. The degree of polarization, P, of the emitted fluorescence is given by

$$P = \frac{I_{11} - I_1}{I_{11} + I_1}$$

where I_{11} and I_1 refer to fluorescence intensities with parallel and crossed polarizers in the excitation and emission channels, respectively. The Perrin equation[79] relates the observed P to the microviscosity of the medium by

$$\frac{\frac{1}{P} - \frac{1}{3}}{\frac{1}{P_0} + \frac{1}{3}} = 1 + \frac{\zeta RT}{V_0 \eta}$$

where P_0 is the degree of polarization in extremely viscous or rigid media, V_0 the effective volume of the molecule, T the temperature, R the gas constant, and ζ the lifetime of the fluorescence. The technique uses the lifetime of the fluorescence as a clock to measure the rate of movement of the probe molecule in the medium. Micellar microviscosities from 10 to 30 cP have been measured by this method.[70,60] A criticism of the method lies in the inability of the experiment to distinguish the actual molecular motion giving rise to the fluorescence depolarization. However, structural changes in vesicles, membranes, living cells, proteins, etc., have been monitored by this technique.[70,80–84]

B. Excimer Formation

An alternative method of measuring micelle rigidity is to use the ability of some excited molecules to form excimers.[72–76,80a] The classic example of excimer formation is that of pyrene, where the long lifetime of the excited state P* provides ample opportunity for interaction with molecules in the ground state P to form excimers P_2*:

$$P \rightarrow P^* \tag{2}$$

$$P + P \rightleftarrows P_2^* \tag{3}$$

The kinetics of the process have been established for simple molecular solvents,[85] the forward reaction of eq 3 being diffusion controlled and occurring at every encounter of P* and P. The monomer emission I_M is observed at $\lambda < 4000$ Å and that of the excimer I_E at wavelengths around 4800 Å. It is common practice to use the ratio I_E/I_M as a measure of the ease of excimer formation or ease with which reaction 3 occurs. As this is diffusion controlled, the rate will vary inversely with the viscosity of the medium. Several liquids of known viscosity are used to produce a calibration of I_E/I_M vs. viscosity. This is then used with measured I_E/I_M in experimental systems to measure the viscosity of the medium. The technique works quite well in homogeneous media, but can be a source of trouble in micelles and vesicles.

In micellar systems the probability of excimer formation depends on a situation where a micelle contains at least double occupancy by pyrene molecules.[77] A micelle containing only one pyrene molecule cannot form excimers, as the second molecule of pyrene cannot contact the single excited molecule during the lifetime of the excited state. Movement from one micelle to another is quite long compared to the excited-state lifetime. However a micelle with two or more pyrene molecules readily forms excimers due to the micellar proximity effect. Hence the distribution of pyrene molecules among the micelles is a controlling factor in forming excimers, while in homogeneous systems diffusion and medium viscosity are all important.

The molecules distribute themselves among the micelles according to a Poisson distribution. The probability of finding a pyrene molecule per micelle is given by P_n where

$$P_n = \frac{\langle Q \rangle^n}{n!} > e^{-\langle Q \rangle}$$

Q is the average number of pyrene molecules per micelle, i.e., $\langle Q \rangle = [P]/[\text{micelle}]$. A simple measure of I_E/I_M in micellar systems does not enable one to interpret the data in terms of viscosity alone. However, direct observation of the rate of decay of P* and formation of P_2* can give a measure of the local movement of P* in a micelle. Figure 2 shows typical curves for P* and P_2* in small spherical micelles and large rod micelles. In small micelles a rapid initial decay of P* is observed which is concomitant with a growth of P_2*; this corresponds to the situation where $n = 1$. For large micelles n is nearly always experimentally >1, and only a rapid single decay of P* and growth of P_2* are observed.

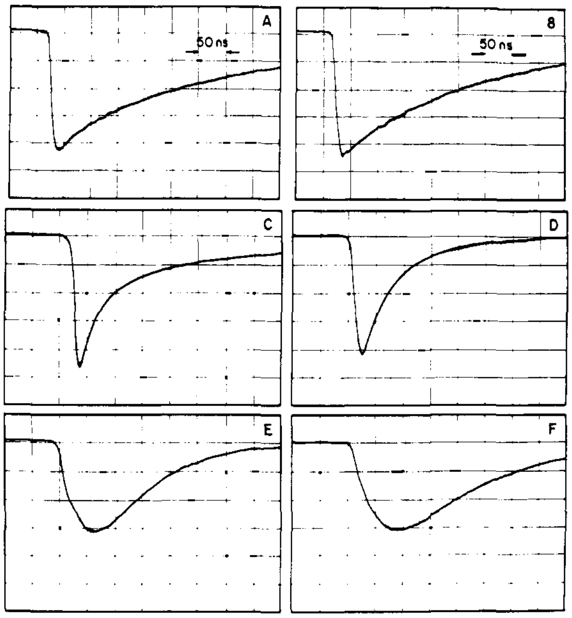

Figure 2. Fluorescence decay of pyrene (ordinate) in spherical and cylindrical micelles: A, [pyrene] = 10^{-4} M, λ 400 nm; B, [pyrene] = 10^{-4} M, [NaCl] = 0.2 N, λ 400 nm; C, [pyrene] = 10^{-3} M, λ 400 nm; D, [pyrene] = 10^{-3} M, [NaCl] = 0.2 N, λ 400 nm; E, [pyrene] = 5 × 10^{-4} M, λ 480 nm; F, [pyrene] = 5 × 10^{-4} M, [NaCl] = 0.2 N, λ 480 nm.

Vesicle systems illustrate yet another problem with regard to excimer formation.[74,88] These large structures readily satisfy the condition $n > 1$. However, the pyrene is often dispersed nonuniformly in these systems. The structures are more ordered than micelles and tend to force the pyrene molecules together forming pyrene aggregates. The excimer P_2^* is mainly formed in these aggregates rather than via random diffusion of P* and P in the vesicle structure. At elevated temperatures, usually above the phase transition, pyrene molecules are distributed more uniformly in the vesicle and normal behavior is then observed for P_2^* formation.

The concept of using excimers to measure local molecular motion in a system is valid provided the system is thoroughly understood and that time-dependent measurements are made in addition to steady-state measurements.

A variation in the foregoing excimer technique is provided by systems where the chromophores are linked together by short methylene chains, O linkages, or N atoms.[77,78] Now, bulk diffusion of the P*,P pair is not required, but a rearrangement or bending of the molecules gives rise to P_2^*.

The bending motion to form A is dependent on the solvent viscosity, and hence a measure of the microviscosity of micelles, and probably other systems, can be obtained with these molecules simply by measuring the ratio excimers/monomer. It would appear at first sight as though the problems normally associated with excimer formation in the unlinked molecules are not present when the chromophores are linked together.

With sufficient care the restriction placed on motion of a probe molecule in an aggregate can be ascertained, a measurement which is important in discussions of reactions in these systems.

IV. Molecule Probe Environment

A. Pyrene Fluorescence Fine Structure

Most molecules exhibit spectral changes in different micellar environments.[87] The underlying explanations for these effects are not always clear, although the actual data may often be useful in a qualitative sense to discuss environment polarity and to monitor structural changes.

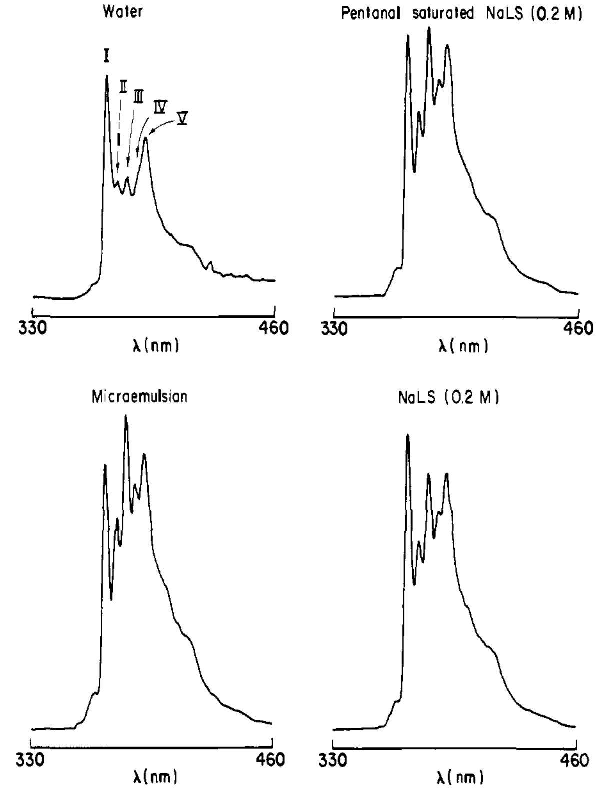

Figure 3. Pyrene III/I fluorescence fine structure, in water; 0.2 M NaLS, pentanol-saturated 0.2 M NaLS; NaLS/pentanol/dodecane microemulsion.

The fine structure of pyrene fluorescence is quite dependent on solvent,[88,89] as shown in Figure 3, where spectra are shown in dodecane, water, NALS micelles, and a NALS/dodecane/pentanol/water microemulsion.[90] Peaks I and III, as marked, show the greatest solvent dependency and may be correlated with medium polarity,[88] although specific, but weak, complexes of pyrene with alcohols[91] and quaternary ammonium groups[92] have been reported. The first singlet absorption of pyrene, ^1A_g, is very weak, although not symmetry forbidden, the $^1B_{3u}$ state being short axis polarized. The fluorescence of the first excited state shows mixed polarization, which is probably due to a mixing of the excited state $^1B_{3u}$ (short axis polarized) with the second excited state $^1B_{2u}$ (long axis polarized). The fluorescence spectrum of pyrene shows vibronic bands corresponding to allowed vibrations (B_{1g}) and forbidden vibrations (A_g), including the 0–0 band. Solvents markedly affect the intensity of forbidden vibronic bands in weak electronic transitions. In the case of pyrene, peak III is strong and allowed and shows little variation with solvent, while peak I (0–0) is forbidden and weak in poor nonpolar solvents. The ratio III/I can thus serve as a measure of the solvent environment surrounding pyrene.

The data in Figure 3 show that the III/I ratio increases markedly on changing solvent environment from water to NaLS micelles, although the III/I ratio is less than that observed in dodecane. This indicates that pyrene experiences an environment somewhere between that of an alkane and water, in agreement with an assignment of the probe to the micellar surface region. Introduction of the cosurfactant pentanol into the head group region of the NaLS micelle displaces pyrene further into the micelle, and the III/I ratio increases. The formation of an alkane/dodecane core in the microemulsion increases the III/I ratio even further, indicating that pyrene now also moves into the hydrocarbon core region. However, the probe is not static as pyrene moves within the microemulsion

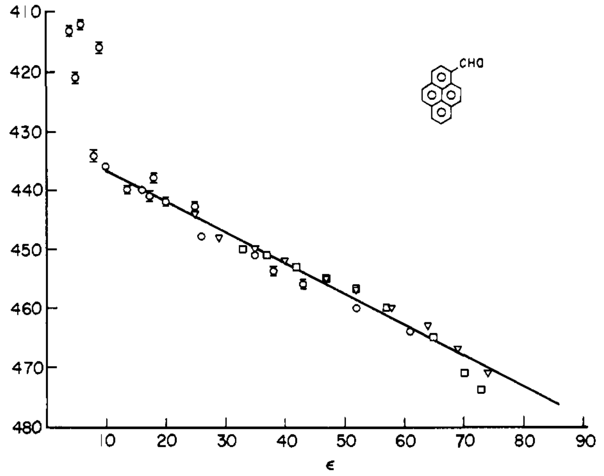

Figure 4. Variation of fluorescence maximum λ_{max} of pyrenecarboxaldehyde with dielectric constant of medium ε.

and also into the aqueous phase. However, the III/I ratio is indicative of the fact that pyrene spends the majority of its time in the alkane environment.

B. Measurement of Micellar Surfaces

Several molecules show spectroscopic behavior indicative of their environment; for example, the absorption spectrum of benzophenone[92] is quite solvent dependent, and the spectroscopic data show that this molecule is located on the micellar surface. This molecule can be used to give a measure of the local polarity of the surface. Similar absorption spectroscopic data with pyridinium ions have been reported where a local dielectric constant of 32–35 was reported for the surface of micelles.[93]

Other polar molecules show quite marked changes in fluorescence spectra under different solvent conditions, e.g., ruthenium bipyridyl ion,[94] which gives a red shift with increasing solvent polarity. Pyrenecarboxaldehyde (PCHO) fluorescence shows a marked red shift with increasing solvent polarity. Figure 4 shows a plot of the wavelength maximum, λ_{max}, vs. the dielectric instant, ε, of the medium which is linear when $\epsilon > 10$. The explanation of this behavior lies in the interplay of two chromophores of the system, CHO and the aromatic pyrene. In nonpolar media the fluorescence maximum lies at $\lambda_{max} \sim 4000$ Å and is due to an $n-\pi^*$ transition. When the polarity of the medium is increased the $\pi-\pi^*$ level, which lies close to the $n-\pi^*$ level, is brought below that of the $n-\pi^*$ by solvent interaction with the excited state, leading to $\lambda_{max} > 4000$ Å.

Figure 4 may be used to measure the local ε in the vicinity of the micelle surface. For example, 0.05 M NaLS has $\epsilon = 45$ compared to 80 of bulk water, and drops to 35 on addition of 0.2 M NaCl. The small ε at the micelle surface is due to the restriction of water molecules at the interface due to the large micellar electric field.

Measurements of the type discussed above give useful information on the nature of different regions of micelles, i.e., the degree of rigidity and polarity of the interior and surface regions. The measurements are often troubled by kinetic motion of the probe molecules used, a feature which is of immediate interest in photoinduced reactions in these systems.

V. *Reactions in Aggregated Systems*

A framework for discussing reactions that one might expect in micellar systems is shown in Figure 5.[95] Four types of processes are depicted in this figure, processes that are directed by, or occur as, a direct consequence of micelles or aggregated systems. The colloidal particle is represented as a spherical object with reactants A, B, or C in different locations with regard to the particle. A point to emphasize in Figure 5 is that at least one of the reactants has to reside with the particle for a major portion of its time.

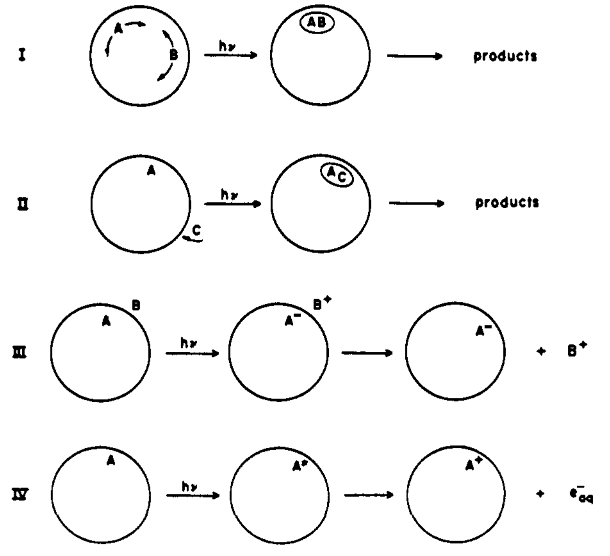

Figure 5. Nature of reactions of A and B in micellar systems.

In case I both reactants A and B reside primarily with the particle and not in the aqueous phase. This is due to their hydrophobic character. Excitation of one of these species by light leads to reaction when the excited species meets with the other reactant. Such a reaction is strongly promoted over that in homogeneous solution, due to the close proximity of the reactants. Several examples of this proximity effect will be discussed subsequently.

In process II the hydrophobic reactant A is with the particle while the hydrophilic reactant C is in the water phase. Excitation of A leads to the excited state A, and for reaction to occur C must penetrate the micelle to A*. In some instances A* is long-lived and may exit the micelle into the bulk phase to react with C, but A* must possess a very long lifetime (≫ μs) for this to occur. Unlike process I, no catalysis is observed, but frequently retardation ensues, and the excited molecule A* is protected from damage by impurities such as C. This effect is readily observed if C and the micelle have the same type of charge, when electrostatic repulsion repels C away from the micelle surface.

A variation of process I is shown in process III, where again both A and B are with the micelle with the added condition that B is only weakly solubilized at the micelle. Excitation by light may lead to electron transfer from B to A, forming A^- to B^+, or A to B depending on the system. This is the proximity effect of process I. If the micellar charge is of the same type as that of B, e.g., CTAB and B^+, then repulsion of B^+ from the micelle occurs leading to efficient separation of A^- and B^+ and prevention of the back-neutralization reaction. Thus light energy is efficiently converted into ionic chemistry and storage of energy results. The charge of the micelle surface may also stabilize one of product ions, e.g., tetramethylbenzidine cation in NaLS, and lead to efficient production of ions.[96]

Process IV is a variation of process III where the electron acceptor is the bulk solvent water. Excitation of the system leads to photoionization, and the electron is observed in the aqueous phase as a hydrated electron, e^-_{aq}. This process is most efficient in anionic micelles, partly due to the prevention of back-reaction of A^+ and e^-_{aq}. A unique feature of this system is the lowering of the energy required to promote the ionization process compared to that in the gas phase.

Processes I to IV are helpful in the subsequent discussion of reactions in aggregated systems.

A. Reactions of Free Radicals

An early example of micellar or emulsion catalysis of a free-radical reaction is that of emulsion polymerization, an important industrial process illustrating reaction type I or the proximity effect. Here a polymerizing free radical and a monomer are held in close proximity in a colloidal particle resulting in enhanced polymerization. For the most part free-radical reactions are influenced only by process I, and the effects depend on the entity involved. Several free-radical reactions initiated in micellar systems by high-energy radiation have been reported,[5] and recently pulse radiolysis has been used to investigate kinetic processes in micellar systems.[97,98]

In some instances the counterion is reactive and may enter into free-radical reactions. It is well established that OH radicals react readily with halide ions X^- to form dihalide radical anions X_2^-. In pulse radiolysis experiments OH radicals are readily produced via

$$H_2O \xrightarrow{H_2O} H_3O + e^-_{aq} + OH$$

$$e^-_{aq} + N_2O \xrightarrow{H^+} OH + N_2$$

high-energy initiation

and the following sequence of steps produces X_2^-.

$$OH + X^- \rightarrow OH^- + X \qquad (4)$$

$$X + X^- \rightleftarrows X_2^- \qquad (5)$$

The Br_2^- formed via this sequence of steps in bromide solutions is readily identified as a strong optical absorption at 365 nm. The kinetics of Br_2^- have been studied both below and above the micellar cmc in CTAB solutions.[99] Below the cmc, Br_2^- is formed via (4) and (5), and the decay

$$Br_2^- + Br_2^- \rightarrow Br_2 + 2Br^- \qquad (6)$$

follows conventional second-order kinetics. Above the cmc, an initial rapid decay of Br_2^- is observed, followed by a subsequent slower one, both reactions following (6), but at different rates. The initial rapid decay of Br_2^- is attributed to reaction of Br_2^- in the vicinity of the micelle, where these species are concentrated by the positive micellar charge. The slower decay is attributed to the bulk reaction of Br_2^-. It is stated that detachment of Br_2^- from the micelle is required for reaction to occur and that the residence time of Br_2^- on the micelle is 1.5 × 10^{-5} s.

Spin traps of the type RN=O have been used to capture radicals to form stable nitroxide radicals, which can be studied at leisure by ESR spectroscopy. Micellar systems have quite remarkable effects on these processes, as shown in Figure 6.[100] This figure shows the generation of a nitroxide radical EPR signal following radiolysis of micellar systems containing a spin trap. Radiolysis of the surfactant/water systems leads to OH radical attack, giving surfactant radicals. These radicals are subsequently captured by the spin trap, giving the nitroxide radicals

$$OH + \text{surfactant (S)} \rightarrow S + H_2O$$

$$S + \quad + t\text{-Bu—N=O} \rightarrow \quad + t\text{-Bu—N—S} \qquad (7)$$

Reaction 7 is not observed below the cmc of micellar NaLS or NaOS (sodium octyl sulfate). However, at the cmc a sharp rise in the yield of nitroxide radical is observed which is attributed to the fact that reaction 7 is relatively slow and does not compete well with other reactions which deplete the surfactant radicals. In micellar solutions, however, the surfactant radicals and the spin traps are localized in one region, namely the micelle, thus bringing process I into action and leading to a promotion of reaction 7. Similar reactions have been observed in lecithin vesicles.[101]

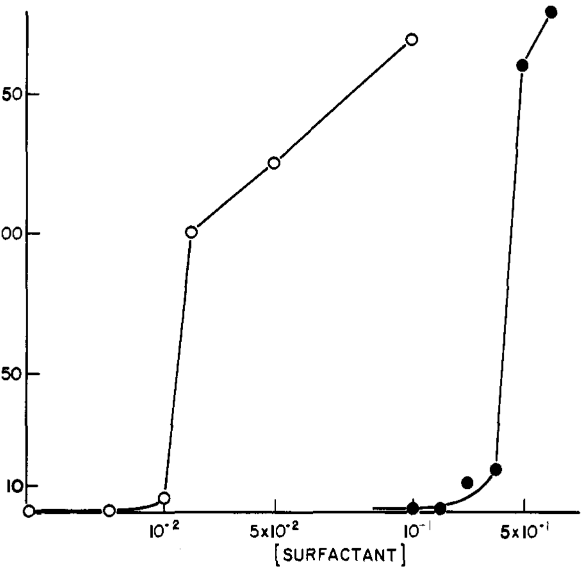

Figure 6. Extent of the reaction $R^0 + RNO \rightarrow R_2NO^0$ in surfactant systems at different concentrations. Abscissa, (○) NaLS, (●) NaOS; ordinate, $[R_2NO^0]$.

Photolysis of aromatic ketones in micellar solutions has been used to obtain ^{13}C, ^{12}C isotope enrichment[102] by utilizing the well-known CIDNP effect. On photolysis of dibenzyl ketone (DBK) in benzene solution, a small but significant $^{13}C/^{12}C$ isotope enrichment occurs which is greatly enhanced in micellar solution. The reactions cited are

$$\underset{\text{DBK}}{PhCH_2COCH_2Ph} \rightarrow \underset{\text{excited singlet}}{PhCh_2COCH_2Ph} \rightarrow \underset{\substack{\text{excited}\\ \text{triplet}}}{DBK^T}$$

$$DBK^T \rightarrow \underset{\text{I}}{PhCH_2CO} + \underset{\text{II}}{CH_2Ph}$$

Radicals I and II subsequently recombine to form DBK. If the radicals are confined to a cage-type environment, e.g., micelle, then process I occurs, due to an enhanced rate of recombination of radicals. As the ^{13}C-containing radicals relax more rapidly than the ^{12}C radicals, then an enriched ^{13}C DKB product is formed. The relaxation of the ^{12}C radicals is much slower, and radicals I and II, recombining in the solution, both give rise to enriched ^{12}C, DBK. The recombination of I and II in the cage must involve a system crossing from triplet character to singlet character in order for stable bond formation to give DBK. The nuclear hyperfine coupling (HFC) in the cage pair I and II is due to the coupling of the odd electron of $PhCH_2CO$ to a ^{13}C nucleus and controls the rate of intersystem crossing of the triplets I and II pair to the stable singlet product. In the absence of HFC the radicals I and II are scavenged or decarboxylated at rates faster than they are converted to product. Hence the DBK becomes enriched in ^{13}C. This is an intriguing feature of reactions in micellar environments which could be of practical importance.

The photolyses of benzophenone and derivatives of benzophenone have been investigated in micellar systems. The object of the work was to promote selected synthetic pathways by means of the micelles.[103] However, no data of use to synthesis have been obtained.

Free radicals formed by OH radical attack on the surfactant monomer may be used to obtain useful information on micellar equilibria. Radiolysis of solutions of the surfactant sodium 4-(6-dodecyl)benzenesulfonate leads to OH attack on the benzene ring, leading to a strongly absorbing species at λ = 3200 Å, which enables one to readily observe the surfactant radical.[97] Below the cmc the radicals dimerize with $2k = 4.2 \times 10^8$ M^{-1} s^{-1}, while above the cmc the rate constant diminishes as radicals become associated with micelles. The rate of association of a surfactant radical with a micelle is measured as 4×10^8 M^{-1} s^{-1}, and the dissociation is 8×10^5 s^{-1}. Similar studies have been carried out with surfactants $C_{16}H_{33}(OHC_2CH_2)_{21}OH$ and $C_{14}H_{29}(OHC_2CH_2)_{23}SO_3Na$. If several radicals are formed in one micelle, then the radical dimerization reaction is catalized due to the local high concentration of radicals, and radical lifetimes of 10^{-6} s or less are observed. This contrasts sharply with free solution where the lifetimes approach milliseconds. Continued irradiation of these systems leads to the formation of polymeric material due to cross-linking of the surfactant molecules.

The rate of association ($k = 1.5 \times 10^9$ M^{-1} s^{-1}) and dissociation ($k = 1.8 \times 10^5$ s^{-1}) of monomer surfactant in NaLS micellar systems has also been measured by a pulse radiolysis technique,[96] where OH radicals were used to generate radicals of the NaLS monomer. These radicals entered into the conventional monomer–micelle equilibrium. In the presence of $K_3Fe(CN)_6$ the rate of association of radicals with micelles competes with the rate of radical reduction of the $Fe(CN)_6^{3-}$ ion, which was observed spectrophotometrically. Radicals in micelles did not react with $Fe(CN)_6^{3-}$ ions due to repulsion of these ions by the negative surface. Analysis of the data produced rate constants quoted above, and also produced data on the association of pentanol and cyclohexanol with these micelles. The equilibrium constant for pentanol–micelle interaction is $K/N = 25$ M^{-1}, where N is the average aggregation number.

B. Photophysical Processes

Many photophysical processes have been studied in micellar systems.[80,104] Table I summarizes some of the systems studied together with the rate data obtained. The simplest observation of excited-state dynamics in aggregated systems has been dealt with earlier, namely fluorescence polarization studies which indicate the restrictional factors controlling movement of the probe molecule. The effect of external factors, such as other solute molecules, on the fluorescence will be discussed in this section. Here, one of the key arguments used is a statement to the effect that the fluorescing molecule is quenched in the aggregate and does not move out into the bulk of the solution in order for quenching to occur. Lifetimes of most fluorescence quenching reactions are less than 3×10^{-7} s, which is evidence in favor of the above statement. Conclusive proof is provided by observing the reactions of long-lived triplet excited states in these systems.

C. Triplet States and Phosphorescence

Triplet states have long lifetimes, thus enabling the observer to extend his probing investigations of a micellar system from 10^{-9} s to seconds. Some early observations on triplet anthracene indicated that the exit time of this molecule from a CTAB micelle was ~1 ms.[105] Indeed micellar systems promote long triplet lifetimes of arenes, a situation that is difficult to match in molecular solvents, e.g., alkanes or arenes. Impurities in these solvents decrease the triplet lifetime whereas micelles protect the solubilized triplet from impurities. Micelles also inhibit triplet-state–ground-state interactions by solubilizing one molecule per micelle. The long triplet lifetimes enable the direct observation of phosphorescence to be made in solution at room temperature.[106,107] The data have been confirmed in other laboratories and extended to other areas.[108,109]

In the first instance the phosphorescence spectra of brominated derivatives of naphthalene, pyrene, and biphenyl were observed. The heavy atom effect of the bromine promotes spin–orbit coupling, giving rise to phosphorescence lifetimes in the millisecond range; much longer lifetimes are still difficult to observe. The phosphorescence of iodo derivatives could not be observed at room temperature as the triplet rapidly decays ($\zeta < 10^{-11}$ s), giving an arene radical and I atom.[110] As an alternative to using brominated derivatives, a heavy atom counterion can be placed on the micelle, e.g., Br^-, I^- on CTAB, or Tl^+ on NaLS. By this technique the phosphorescence of the unsubstituted arenes was observed. The heavy ion increases the rate of the triplet-state–ground-state radiative transitions, giving use to a greatly enhanced phosphorescence in the millisecond time region. This is an example of the proximity effect, as triplet and heavy ion are held together by the micelle. An effect similar to this may also be observed in fluid solution if a brominated solvent, e.g., (CH_2BrCH_2Br), is used.[108]

The arene phosphorescence provides a convenient method of investigating the rates of entry and exit of these molecules in micellar systems. For example, a molecule such as bromonaphthalene, NB, is excited in micellar NaLS and the rate of decay of the phosphorescence noted (eq 8). In the presence

$$NB \rightarrow NB^S \rightarrow NB^T \xrightarrow{k_0} NB + \text{phosphorescence} \qquad (8)$$

of NO_2^- ion the rate of decay of the phosphorescence is much faster and increases with $[NO_2^-]$.

$$NB^T + NO_2^- \rightarrow NB + (NO_2^-)^* \qquad (9)$$

In homogeneous solution the reaction of $NB^T + NO_2^-$ is diffusion controlled. In micellar systems two processes compete, namely the rate of quenching NB^T by NO_2^- and the rate of reentry of NB^T into micelles (eq 10). Once associated with an NaLS

$$NB^T + \text{micelle} \rightleftarrows (NB^T, \text{micelle}) \qquad (10)$$

micelle, NB^T is protected from attack by NO_2^- due to electrostatic repulsion. Thus the lifetime of NB^T in the micellar system decreases with $[NO_2^-]$ to a plateau where the rate of reaction 9 is much greater than that of 10 and the limiting lifetime is that of exit of NB^T from a micelle to the bulk phase. A full analysis[55] of the kinetic data gives the rates of exit and entry of the triplet out of and into micelles.

The measured exit times are long (~1 ms) for many molecules but depend on the actual molecule. The ratio of rates of process 10, i.e., k_{10}/k_{-10}, is the distribution constant of probe between micelle and bulk water. This ratio is readily measured from solubility studies as k_{10} is close to diffusion control and can be estimated by diffusion theory. Hence, the exit rate k_{-10} is conveniently calculated from solubility data. It is found that the logarithm of the solubility of an arene in a micellar system varies with the boiling point of the arene and provides a rough guide for calculating solubility data in the absence of other direct measurements.

D. Fluorescence

Earlier sections indicated the unique effects of micellar environment on the fluorescence spectra of many probe molecules, e.g., pyrene, pyrenecarboxaldehyde, *N*-phenylnaphthylamine, etc. Pyrene, due to its long fluorescence lifetime (>300 ns), is a particularly useful probe in studies of reactions of excited states. Probably the simplest reaction is that of excimer formation (eq 3), which was studied for pyrene and 2-methylnaphthalene.[111] In an aqueous colloidal system, pyrene is confined to the hydrophobic environment of the micelle, vesicle, etc., and high local probe concentrations promote the proximity effect I. In small colloids such as micelles the controlling factor in excimer formation is the distribution of the probe among the micelles. It is suggested that probe molecules distribute themselves among the micelles according to a Poisson distribution, although an alternative distribution has been suggested.[112,113,114]

TABLE I: Rate Constants (M^{-1} s^{-1}) for Reactions in Micelles[a]

reaction	water or alcohol	NaLS	NaTC	NaTC/3% cholesterol	sodium oleate	CetMe$_3$NBr	Brij 35	Igepal Co 630	Triton X-100	bilayer distearyl-lecithin	lysolecithin 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$_3$NO$_2$	8.1	3.0	0.12			1.8	1.7	0.53	0.51	0.055	0.57
Py* + Cu^{2+}	20.0	$r < 5 \times 10^8$ s^{-1}				$<10^{-3}$ 4.2×10^{-2}	2.7				
Py* + 1	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)	66	0.54	0.40	0.69	$<10^{-2}$	0.51
Py* + triethylamine	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		$r < 6 \times 10^{-8}$			3.1×10^{-2}		0.16	0.22	$<10^{-3}$	0.39
Py* + Cu^{2+}		6.7									
Py* + methyl viologen		7.2									
Py* + cetylpyridinium chloride		7.4									
Py* + P		(9×10^{-3} s^{-1})									
Py* + P		1.7×10^{-2} s^{-1}				1.2×10^{-2} s^{-1} 4.5×10^{-3} s^{-1}					
PBA* + PBA						1.0×10^{-2} s^{-1}					
PBA* + 1$^-$		0.5									
Py* + RNO		1.5×10^{-2} s^{-1}									
bromonaphthalene* + Eu^{3+}		5×10^{-4}									
Tb^{3+}		1.8×10^{-4}									
bromobiphenyl* + Tb^{3+}		4.5×10^5									
duroquinone^T + DPA		6×10^6 s^{-1}									
OH		7.6 (monomer) 0.5 (micelle)									
OH + Py											
OH + benzene		~2				~3				1.7	
H		1.2×10^{-2} (monomer and micelle)				1.6×10^{-2} (monomer and micelle)					
H + biphenyl	6.0	6.0				6.0					
O$_2$* + α-tocopherol (singlet O^2)		0.64									
e$^-$ Transfer											
Py* + DMA	>1.0 s^{-1}	>1.0 s^{-1}				>1.0 s^{-1}					
Cu$^+$ + (methylphenothiazine)$^+$		9.0 s^{-1}									
Ni^{2+} + (methylphenothiazine)$^+$		2.1×10^{-2} s^{-1}									
Co^{2+} (Methylphenothiazine)$^+$		4.2×10^{-2} s^{-1}									
Eu^{2+} (methylphenothiazine)$^+$		~10^{-2} s^{-1}									
(RuP^{2+})* + methylphenothiazine		3×10^{-4} s^{-1}									

[a] Some rate constants are given in units of s^{-1} when the reactants are both in the micelle and the concentration is uncertain. From references shown and 86, 101, 116, 121, 129, 158. [b] 4×10^{-2} M MgCl$_2$. [c] 0.2 M benzyl alcohol. [d] 0.1 M NaCl. [e] Rod, micelle. [f] Limiting τ of reaction at high [solute].

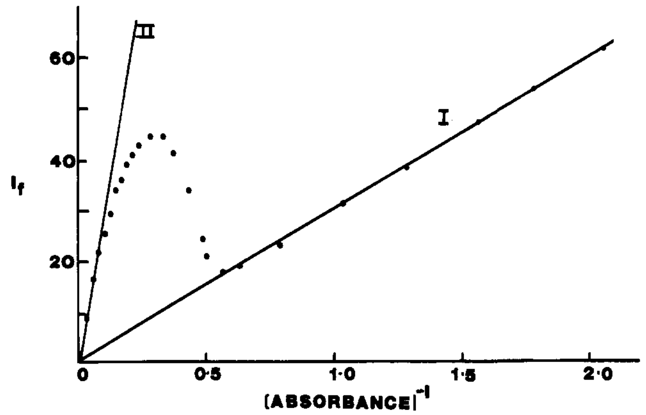

Figure 7. Energy transfer from phenyl group of phenylundecenoic acid to naphthalene. Ordinate, fluorescence of naphthalene; abscissa, inverse of absorbance of solution.

In larger colloids, e.g., vesicles and microemulsions, there are usually more than one probe molecule/particle.

E. Energy Transfer

The proximity effect type I induced by micelles leads to efficient energy-transfer processes. Such effects have even been suggested to have utility in liquid dye laser systems.[116] Micelles also provide useful vehicles for studying energy-transfer processes of interest in photosynthetic systems: both chlorophyll *a* and *b* have been solubilized in micelles up to concentrations equivalent to those in photosynthetic membranes.[117,118] Efficient energy transfer from methylene blue to thionine has been observed in anionic micelles, where each acceptor seems to quench 5–7 donor molecules.[119,120] Nonionic micelles of the Triton series have a phenoxy chromophore in the surfactant, and efficient energy has been observed from this chromophore to solubilized pyrene.[121] Several arenes, such as naphthalene and biphenyl, in anionic micelles transfer energy to counterions such as Eu^{3+} and Tb^{3+}, and the luminescence of the Tb^{3+} has been observed in these experiments.[122,123] Many of these reactions are quite slow in the absence of micelles and cannot be observed in homogeneous solution; hence, a large micellar catalytic effect is induced via process I.

A good example[124] of the subtleties of energy transfer in micellar systems is shown in Figure 7 for a host micelle, comprised of the surfactant sodium phenylundecanoate with naphthalene as the guest molecule. The intensity of the naphthalene fluorescence is shown at constant [naphthalene] and varying [surfactant], plotted vs. the reciprocal total absorbance at the excitation wavelength. At low [surfactant] the naphthalene fluorescence decreases as light is absorbed by the phenyl group of the surfactant. At the cmc, the fluorescence suddenly increases as the probe is incorporated into the micelles in close proximity to the excited phenyl group, thus giving rise to efficient energy transfer. At higher concentrations, the [micelle] increases beyond that of the naphthalene, and the efficiency of energy transfer decreases. In this system, the phenyl group might be looked upon as an antenna molecule which increases the amount of energy centered on the guest molecule naphthalene.

F. Quenching Reactions

The energy-transfer processes discussed above lead to quenching of excited states in micelles, and the systems are static as in type I. A more general case is a situation where the quenching molecule moves freely in both micelles and bulk phase while quenching still only takes place when excited state and quencher are in the same micelle. If the quenching molecule is present in a micelle at the moment of probe excitation, then rapid quenching can ensue, although it is also possible that the quencher may exit the micelle without quenching taking place. If the quenching molecule enters the micelle following probe excitation, then the rate of quenching is primarily controlled by this process. The system pyrene CH_2I_2/NaLS illustrates the above behavior, where an initial rapid quenching of excited pyrene is followed by a slower one,[125–127] as defined by the processes discussed above. The kinetics of the system have been worked out in detail,[125–127] and the rate constants of entry, exit, and quenching of excited pyrene by CH_2I_2 are found to be $k(\text{entry}) = 2.5 \times 10^{10}$ M^{-1} s^{-1}, $k(\text{exit}) = 9.5 \times 10^6$ s^{-1}, and $k_q = 7.5 \times 10^7$ s^{-1}. For the quencher CH_3NO_2, which is polar and has a low affinity for hydrophobic micelles, the quenching condition approximates to 1 where CH_3NO_2 moves rapidly into and out of the micelle, but no significant micellar residence time exists. Thus quenching is via entry of CH_3NO_2 into a micelle containing excited pyrene. This simple condition is often aimed for in order to avoid the complication of more than one type of kinetics for the quenching process.

At first sight the solubility of a neutral entity in a micelle might be ascertained from its solubility in alkanes. Some modifications of this concept are necessary in discussing quenching reactions. For example, O_2 has a much higher solubility in organic solvents than in water, and one would expect a higher $[O_2]$ in a micelle than in the aqueous phase, a condition which is found experimentally. However, under 1 atm of O_2, many micelles do not contain an O_2 molecule. For example, 0.1 M NaLS gives rise to a [micelle] $\sim 2 \times 10^{-3}$ M while the $[O_2]$ associated with this amount of surfactant is $\sim 3 \times 10^{-4}$ M, which leads to a situation where O_2 per micelle is <1. However, O_2 moves freely in and out of micelles, leading to quenching of micelle-bound excited states. In larger colloids, such as microemulsions, where the particle approaches more nearly the concept of an oil drop in water, then the resident $[O_2]$ in the particle is close to that observed in alkanes and some fourfold that in water.[128] The relative degree of solubilization in the colloid and the bulk phase are of great concern in discussions of quenching reactions induced by photochemical processes.

The kinetic situation is somewhat simplified in large colloidal particles such as microemulsions. In these systems, the proximity effect increases the rate of reaction over that in homogeneous solution by a factor *S*, which is the ratio of the volume of the total solution to that of the microemulsion phase. In other words, simple concentration considerations apply as these systems have little internal structure and low viscosity. By contrast, in micellar systems the reactants are located more in the surface region where they experience structural details of the head groups. The rigidity of the head-group region decreases the mobility of the reactants, but the proximity effect still increases the observed reaction rate over than in homogeneous solution. These considerations apply primarily to diffusion-controlled reactions. For reactions that are not diffusion controlled, the increased rate of reaction can be more dramatic in both micellar and microemulsion solutions. Table I shows that the micellar phase decreases the rates of quenching by hydrophilic quenchers such as O_2, CH_3NO_2, and triethylamine. The data are expressed as rate constants calculated from the observed rate of reaction and the [quencher] expressed in M. No attempt is made to express a local [quencher] in the micelle. Hence, larger rate constants compared to homogeneous solution are calculated in this way for micelle-bound reactants.

Charged quenchers, e.g., Tl^+ or I^-, show increased rates of quenching of excited pyrene, P*, if the micellar systems have the opposite charge to that of the quencher. This arises from absorption of the ionic quencher on the micelle surface in place of the regular counterion, e.g., Tl^+ for Na^+ in NaLS and I^- for Br^- in CTAB. This leads to abnormally high concentrations of

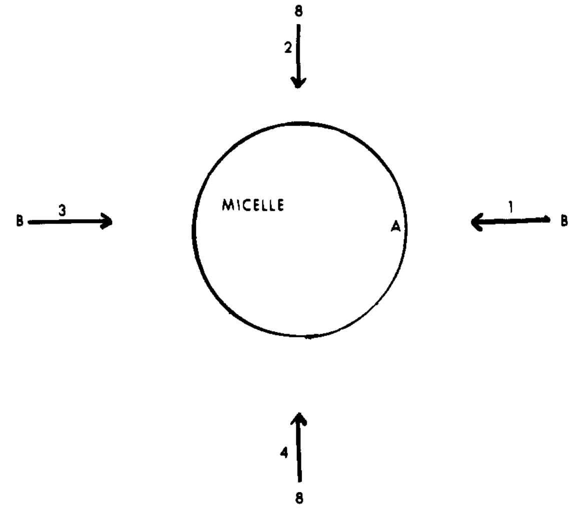

Figure 8. Representation of steric effect of micelle on reaction between A and B.

reactants at the micelle surface. If the micelle and ionic quencher have the same charge type, then inhibition of reaction is observed due to electrostatic repulsion of the quencher by the micelle from the vicinity of P*. Increasing the ionic strength of the solution decreases the repulsion and leads to increased rates of quenching.

Another feature that has to be considered for the preceding reactions is a steric effect imposed by the micelle on the reaction. Figure 8 illustrates this pictorially for reaction A with B which is thwarted by approach of B from positions 2, 3, and 4, only position 1 leading to reaction. An estimate of this steric factor can be obtained from the surface area of the micelle (~1200 Å^2) and the area of the reactants (~75 Å^2), which leads to a steric factor of 1/16. Such simple considerations do not take into account successive collisions of B with the micelle whereby A and B react. Data in Table I show that the rates of quenching of P* by hydrophilic noncharged quenchers are slower than those in homogeneous solution, the effect becoming more apparent with large micelles such as CTAB, Brig 35, Igepal 60-630, and Triton X100.

The addition of divalent inert salts to ionic micelles tends to increase the rigidity of the micelle surface as the divalent ions tend to bind to the surface of the micelle more rigidly than the surfactant counterion. Fluorescence polarization studies confirm an increase in micellar rigidity on addition of divalent salts. For several quenchers, the increased rigidity correlates with a decrease in the rate of quenching.[129] The addition of an alcohol such as benzyl alcohol or hexanol leads to a disruption of the micelle surface as these cosurfactants locate in the head-group region and force the head groups apart. This leads to a loss of rigidity of the surface, which again is reflected in a decrease in the fluorescence polarization of probes in these systems and an increase in quenching by neutral quenchers which gain access more readily to P* under these conditions. Ionic quenchers, e.g., Tl^+ on NaLS, show a decrease in quenching efficiency as the cosurfactant tends to push the pyrene further into the micelle, and away from the surface.

G. Charge-Transfer Reactions

Micellar systems are excellent vehicles for promoting electron-transfer reactions. The micelle provides solubilization of the reactants in close proximity, which provides rapid electron transfer on excitation. The correct choice of micellar surface charge subsequently directs the progress of the ions formed and can enhance separation. In some instances a micellar environment can be used to investigate the molecular site of electron transfer.[130] For example, electron transfer between the electron doners silver(II) protoporphyrin or tetracetylporphyrin and the acceptors $IrCl_6^{2-}$ or $Os(bpy)_3^{3+}$ is inhibited in both anionic NaLS and cationic DTAC. This is explained by blocking the side of the porphyrin ring with the vinyl groups of the protoporphyrin inside the micelle and stacking the propionic acid groups in the stern layer. In such an arrangement the edges of the porphyrin ring, which can transfer electrons, are situated inside the micelle, and electron transfer is more difficult.

It is well established that amines quench excited states of arenes, the product being an excited complex or exiplex in nonpolar media and ions in polar media (eq 11). The system

$$A^* + \text{amine} \rightarrow A^- + \text{amine}^+ \qquad (11)$$

pyrene/dimethylaniline has been studied in micellar systems,[131] the products being pyrene anion, P^-, and dimethylaniline cation, D^+. The products are formed rapidly within the laser pulse in all micelles while the lifetime of the ions is very long (>1 ms) in cationic micelles and is short (<1 μs) in homogeneous solution, as no barrier exists to neutralization of the ions.

Several other systems show similar enhanced effects in micellar solutions:

Excitation of aminopyrene, AP, and benzoquinone, BQ, in NaLS gives rise to AP^+ and BQ^-.[135]

Excitation of zinc tetraphenylporphyrin, ZnT, and methyl viologen, MV, or anthraquinonesulfonate, AQ, gives MV^+ or AQ^- which are stable and are observed by EPR or absorption spectroscopy. The presence of the surfactant is important for such long-lived stability.

A reaction of current importance in these systems is the photoredox system containing ruthenium tris(bipyridyl), RuP_3^{2+}, and an electron acceptor, e.g. methyl viologen.[139,142] Excitation of RuP_3^{2+} leads to electron transfer to MV^{2+} and to the formation of RuP_3^{3+} and MV^+. The RuP_3^{3+} is removed from the reaction sphere by electron donation from ascorbic acid or cysteine which leads to RuP_3^{2+} and a stable radical of the donor; the MV^+ is stable under these conditions. Micellar systems aid in the initial stages of the electron transfer process and also in subsequent charge separation. Catalysts present in the system convert MV^+ to H_2 and MV^{2+}, and such systems are at least models for solar energy storage.[50,51]

Electron transfer is aided by polar environments such as water. Micelles provide a means of solubilizing hydrophobic entities such as chlorophyll or porphyrins in aqueous systems and also help to organize molecules in close proximity to facilitate efficient electron transfer.

H. Photoionization

An even simpler electron transfer process is strongly enhanced by micelles, that of electron transfer to solvent or photoionization. It was ascertained some time ago[143,144] that pyrene could be photoionized in several solvents to pyrene cations and that solvated electrons were produced. Increasing polarity leads to an increase in the yield of photoionization, the greatest yield being observed in micelles.

The increasing yield of photoionization was subsequently shown to be due to more efficient escape of electrons from the photoformed ion pair, the probability of escape increasing with solvent polarity.[147] In the case of micelles the pyrene cation remains with the micelle, while the electron is ejected into the solvent phase and is observed as a hydrated electron. The negative micellar surface interposes a barrier between P^+ and e^-_{aq} which leads to efficient charge separation and long-lived ions.

Micellar systems also reduce the energy required for photoionization.[148] Phenothiazene[149] and tetramethylbenzidine[150] are both photoionized by one photon of 3471-Å light, the onset for photoionization being ~3.0 eV compared to ~6.5 eV in the gas phase; aminoperylene[151] is photoionized by green light

TABLE II. Rate Constants for Reaction of e^-_{aq} (10^9 M^{-1} s^{-1})

solute	homogeneous soln	NaLS	NaTC	CTAB	Igepal	Triton	lysolecithin	distearyllecithin
micelle		$<10^{-4}$ (5, 116)		$<10^{-3}$ (5, 116)	1.7×10^{-2} (5, 116)	3.8×10^{-2} (5, 116)	3.9 (86)	$<10^{-3}$
pyrene	10 (116)	$<10^{-2}$ (116) 4.8×10^{-2} (0.2 M NaCl)	0.13 (158)	>102 (155)	1.7 (121)	2.0 (121)	3.8 (86)	$<10^{-2}$ (101) fast (187)
biphenyl	5.0 (116)	0.13 (116)			3.8 (121)	4.0 (121)		0.005 (101)
pyrene-carboxaldehyde	16 (101)	2.5 (101)						
aminopyrene	14 (101)	1.1 (101)						
benzophenone	10 (5)	1.5 (5)		20 (5)		2.0 (5)		
nitroanthracene	10	1.5 (204)		90 (204)				

(2.4 eV) in NaLS micelles but not in other systems. The photoionization potential, P_s, in solution is related to that in the gas phase, P_g, by

$$P_s = P_g + P_+ + V_0$$

where P_+ is the polarization energy of the cation (~−2.0 eV) and V_0 is the energy of e^- in the solvent (~−2.0 eV) for water. The net reduction in ionization potential can thus be about −4.0 eV compared to that in the gas phase. In this case a micelle provides a suitable environment for a molecule, as maximum solvation energy can be utilized by the ionic products.

I. Reactions of Hydrated Electrons

Hydrated electrons, e^-_{aq}, may be produced in micellar systems by solute photoionization, or via radiolysis of the water bulk.[152,153] These species react rapidly with many solutes, and the reactions may be looked upon as electron transfer solvent to solute. Micellar systems show marked effects on these reactions. It was noted quite early that anionic micelles dramatically retard (~$^1/_{1000}$) the rates of reaction of e^-_{aq} with solutes solubilized in these micelles. Typical of these reactions is e^-_{aq} + pyrene which has $k = 10^{10}$ M^{-1}/s^{-1} in homogeneous solution but has $k < 10^7$ M^{-1}/s^{-1} in NaLS micelles. More polar derivatives of pyrene, e.g., aminopyrene and pyrenecarboxaldehyde, are more reactive than pyrene, and e^-_{aq} reacts with these solutes with $k \sim 10^8$ M^{-1}/s^{-1}. Reactions of e^-_{aq} with Cu^{2+} and Cd^{2+} [155] are diffusion controlled in water but drop some 100-fold when Cu^{2+} or Cd^{2+} is bound to NaLS micelles.[155] Similar data are reported for RuP_3^{2+} [156] and MV^{2+} [151] in NaLS micelles. These effects are due to electrostatic repulsion of e^-_{aq} away from the micellar surface and the vicinity of the solute. More polar solutes lie closer to the micellar surface, which facilitates reaction with e^-_{aq}. Addition of inert salt increases the rate of reaction, as expected by the above mechanism.

Quite contrary results are obtained in cationic micelles such as CTAB, where marked acceleration of reaction of e^-_{aq} and solute is observed due to attraction of e^-_{aq} by the positively charged surface.[159] In cationic micelles such as cetylpyridinium chloride, which is itself reactive with e^-_{aq}, $k(e^-_{aq}$ + micelle$) > 10^{12}$ M^{-1}/s^{-1}.[160] Nonionic micelles reduce the rates of reaction of e^-_{aq} with solutes some tenfold,[5,161] probably due to a steric type effect discussed earlier. These data are shown in Table II.

Reversed Micelles

Certain surfactants such as hexadecylbenzyldimethylammonium chloride,[162,163] BDC, dodecylamine propionate,[164] and diisooctyl sodium sulfosuccinate, AOT,[165,166] form what are called reversed micelles in hydrophobic solvents. A typical spherical structure is shown in Figure 2, where the bulk solvent is heptane or benzene, the surfactant is AOT, and the micelle core contains water. These are three-component systems, unlike regular micelles which are two component, and hence reversed micelles may also be called microemulsions of water in oil. In the AOT micelle shown, some of the Na^+ counterion (<28%) may be dissociated from the head group into the water phase. Fluorescence,[29] proton, and Na NMR[30] show that the physical properties of the water bubbles approach that of bulk water only beyond 1% water (in 3% AOT/heptane). This is a stage where there are more than six H_2O molecules per Na^+. These systems show marked catalytic effects on thermal reactions[164] and appreciably modify radiation-induced reactions. Studies with photoactive probes such as pyrenesulfonic acid[162] and hydroxypyrenetrisulfonate[163] show that the former probe locates at the micelle interface with the pyrene chromophore toward the hydrocarbon phase, while the extremely polar trisulfonate probe tends to lie more into the water sphere. Fluorescence polarization studies[29] show that the micelle is quite rigid at low water content but tends to become more fluid at higher water content. The sizes of the water bubbles are well-known[165,166,168] at various water contents, varying from 15 Å at 0.5% water to 84 Å at 6% for the system 3% AOT/heptane.

Stop-flow studies[167] show that reactants solubilized in the water pools are exchanged between micelles via micellar collision and not via micelle exit to the hydrocarbon followed by capture by other micelles as with regular micelles.[55] Photoinduced studies[32] (data shown in Table III) show that increasing micelle size and water content tend to increase the rates of reaction, where two reactants are hydrophilic and located in the water pool. Examples of such system are quenching of excited PSA by I^-, Cu^{2+}, Tl^+, and nitromethane and electron transfer from biphenyl anion to Cu^{2+}. This is attributed to enhanced mobility of hydrophilic solutes with increasing water content; fluorescence polarization measurements support this suggestion. If a quenching ion is cationic and binds to the anionic micelle surface, then greatly enhanced rates are observed with increasing water content only if the other reactant is also hydrophilic. If the other reactant is hydrophobic and located mainly in the alkane phase, then increasing water content decreases the rate of reaction. This is due to a decrease in the probability of reactant encounters, solely due to the lack of penetration of the hydrophilic reactants into the micelles. Examples of such systems are quenching of excited pyrene by I^- and Cu^{2+} and excited PSA by CH_2I_2.

Reversed micelles are selective in ion separation; for example, photoinduced e^- from ruthenium bipyridyl to benzylnicotinamide (BN^+) in DAP/benzene/water reversed micelles leads to BN which is more hydrophobic than the parent ion and escapes into the bulk hydrocarbon. The net result is storage of light energy as reactive chemical products.[169] Similarly, photoinduced

TABLE 111. Bimolecular Rate Constants[a] (M^{-1} s^{-1}) of Some Reactions Taking Place in the Reversed Micellar System, 3% AOT/H_2O/Heptane

reactions	6% H_2O	3% H_2O	2% H_2O	1% H_2O
$\phi_2^- + PSA \rightarrow \phi_2 + PSA^-$	1.05×10^{10} (6.3×10^8)	1.84×10^{10} (5.5×10^8)	3.7×10^{10} (7.4×10^8)	
$\phi_2^T + PSA \rightarrow \phi_2 + PSA^T$	6.10^9 (3.6×10^8)	7.5×10^9 (2.25×10^8)		6.5×10^9 (6.5×10^7)
$\phi_2^T + PBA \rightarrow \phi_2 + PBA^T$	6.4×10^9 (3.8×10^8)			
$\phi_2^T + Py \rightarrow \phi_2 + Py^T$	2.7×10^{10}			
$\phi_2^T + PTSA \rightarrow \phi_2 + PTSA^T$	$<2 \times 10^9$			
$H_3O^+ + \phi_2^- < \phi_2H + H_2O$	5×10^9 (3×10^8)	5.8×10^9 (1.78×10^8)	4.6×10^9 (9.2×10^7)	4.7×10^9 (4.7×10^7)
$Cu^{2+} + \phi_2^-$ $Cu^+ + \phi_2$	6.3×10^9 (3.78×10^8)	3.0×10^9 (1.1×10^8)	3.4×10^9 (7.9×10^7)	1.7×10^9 (1.7×10^7)
$PSA^* + O_2$	4.6×10^{10}	5.2×10^{10}		5.2×10^{10}
PSA^* Cu^{2+}	2.2×10^{10}	1.5×10^{10}	1.1×10^{10}	3.0×10^9
$PSA^* + Tl^+$	2.0×10^{10}	8.0×10^9	1.2×10^{10}	3.0×10^9
$e^-_{aq} + O_2$	2.0×10^{10}			
DAP reversed micelles in C_6H_{12}[122,189,211]			$k = 2 \times 10^{12}$ in 0.3 M H_2O decreasing to 7.7×10^{10} in absence of water	
$PSA^* + Br^-$			$k = 8.7 \times 10^7$ in 5.5×10^{-2} M H_2O 1.97×10^6 in 4.4×15^1 M H_2O $k = 2.89 \times 10^8$ in absence of water $= 1.25 \times 10^7$ in 0.3 M H_2O	
$+ TbCl_3$			$k = 3.0 \times 10_5$ in absence of water	
In BHDC/Benzene Micelles				
$PSA^* + PSA$			$k = 1.7 \times 10^8$ M^{-1} s^{-1} (212)	

electron transfer from zinc tetraphenylporphyrin to either MV^{2+} giving MV^+ or anthraquinonesulfonate (AQS) only takes place efficiently in micelles of opposite charge to the acceptor, i.e., AOT for MV^{2+} and BDC for AQS. This is a consequence of solubilization of ZnT at the micelle surface or in the hydrocarbon. The excited triplet of ZnT, which is responsible for electron transfer, does not penetrate into the water bubble, and the acceptors have to approach the surface from the aqueous phase for reaction to occur. The acceptors experience electrostatic effects which either promote or retard reaction.

Electron capture by the water bubbles depends on the percentage of water in the system.[32,171] In pulse radiolysis e^- are produced in the hydrocarbon bulk, and some e^- are captured by the AOT water bubbles as e^-_{aq}. Competition studies indicate an extremely rapid rate of e^-_{aq} capture by the bubbles; and it is not certain as yet whether the process involves rapid transfer of thermolyzed electrons to the water pools or whether the pools efficiently thermolyze e^- for subsequent capture and solvation. Photoionization in the bulk hydrocarbon of pyrene does not lead to significant e^- capture. However, pyrene derivatives such as aminopyrene, pyrenebutyric acid, or pyrenesulfonic acid attach to the micelles, and large yields of photoproduced e^-_{aq} are observed.

Reversed micelles act as microcosms for polar or ionic reactions and simulate conditions prevailing in some regions of cell membranes.

Microemulsions

Microemulsions are emulsion systems of small dimensions (<1 μm) formed by a system of at least three components. Basically reversed micellar systems are microemulsions of water in oil. Microemulsions differ from emulsions systems in three important points: they are optically clear, although they scatter light, and are thermodynamically and kinetically stable. The microemulsion systems of main interest in this section are formed by a four-component system, of oil, surfactant, cosurfactant, and water. The systems discussed will be of the oil-in-water type and consist of a hydrocarbon core surrounded by, and separated from, the water bulk by a layer of surfactant and cosurfactant. They were originally suggested and studied by Schulman and co-workers[172,173] and have been extensively studied since this time[174–177] as they are of prime interest in the detergent industry.

To date, few reactions have been studied in these systems, although their very nature will, in the future, provide intriguing suggestions for catalysis of many systems. Mackay and coworkers have studied several inorganic systems in microemulsion systems.[178–180] A few examples of photochemical reactions are also available. Mackay and Jones[161] have used microemulsion systems consisting of sodium cetyl sulfate, pentanol, mineral oil, and water to study the photochemical behavior of chlorophyll with added oxidants and reductants. The chlorophyll is located in the surface region, and undergoes slow photodegradation and slow dark pheophytinization. The photoreaction is accelerated by added oxidants, e.g., duroquinone, while the presence of ascorbate ion protects the chlorophyll. Laser flash photolysis has been used to investigate similar redox systems.[162] It was found that excitation of diphenylamine (DPS) in the presence of duroquinone (DQ) rapidly leads to DPA^+ and DQ^-. In a similar fashion, excitation of the system methylphenothiazine/methyl viologen in microemulsions leads to the cation of the phenothiazine and reduced methyl viologen. These early data indicate that microemulsions facilitate several photoinduced redox processes.

At this stage it is important to ascertain with certainty the locality and environment of solutes in these systems. Studies of this kind have been carried out in a fashion similar to that already published in micelles.[183] An issue of *The Journal of Physical Chemistry* will appear in 1980 with a collection of papers concerned with photochemistry in microemulsions.

Vesicles

Vesicles, a typical pictorial example of which is shown in Figure 1, are colloidal systems which most nearly resemble biomembranes. They are usually made of biomaterials such as lecithins,[38–41] although recently vesicles have been made from synthetic surfactants.[42–44] The necessary criterion for forming a vesicle structure rather than a micelle is geometric,[46] and a rule of thumb is that single-chain surfactants, e.g., CTAB, form micelles, while double-chain surfactants, e.g., dioctadecyldimethylammonium bromide, form vesicles. These structures enclose an inner region of water from the bulk water by forming a closed bilayer structure with the hydrophobic moieties in the interior of the bilayer while the polar groups are in contact with interior water on one side and with bulk water on the other. The structures are large (γ ~ 250 Å), and multilayer liposomes may also be formed under certain conditions.

Some materials, e.g., Na^+, Cl^-, etc., may be trapped in the interior water pool for many days, depending on the conditions of the systems. The hydrocarbon moieties are partially organized, as illustrated by laser Raman studies,[61,71] and fairly viscous, as shown by fluorescence polarization studies.[70,185]

Many vesicles show abrupt changes in physical properties, light scatter, fluorescence polarization, volume, uptake of probe, hydrocarbon chain ordering, pyrene excimer formation, etc., at a set temperature which depends on the actual lecithin or surfactant used. It is customary to associate these observations with a phase changes in the vesicle, the exact nature of which is not exactly known, although many suggestions have been made.

Excimers of pyrene have been used to study movement of molecules in vesicles.[74,75,86,115] Above the phase change of the vesicle, the excimers are formed via a diffusion-controlled process with diffusion constants in the 10^7 cm^2 s^{-1} region. However, below the phase change,[74] a large fraction of the excimers are formed very rapidly and are attributed to regions of high local pyrene concentration. This is confirmed by rapid observations of the P_2* formation which is complete in a few seconds and independent of [P]. Above the phase change the rate of formation of P_2* is much slower than that below the phase change. The III/I pyrene fluorescence fine structure[115] gives a quite polar environment for the molecule in lecithin vesicles which, however, abruptly changes to a less polar environment at the phase change. This is probably due to a localization of pyrene in the head-group structure of the lecithin below the phase change, probably at the water/vesicle interface, much like that in micelles. It is probable that the rigid organized hydrocarbon chains exclude pyrene. Above the phase change, the loss of order in the chains leads to increased solubilization of pyrene into the lipid interior. Pyrene triplet–triplet annihilation has also been observed and gives a diffusion constant of the same order as that observed with P_2*.[186]

Pyrene in vesicles has also been used to study radiation-induced reactions of OH radicals,[101] hydrated electrons,[101,187] and several simple quenchers such as O_2, CH_3NO_2, I^-,[73] etc. The effects observed are much like those observed in neutral micelles with the following limitation on the observed kinetics: In the case of OH and e^-_{aq} reactions, the pyrene is located entirely in the vesicle so the rate-limiting step is the rate at which e^-_{aq} and OH react with the vesicle, where many pyrene molecules are solubilized. Hydroxyl radical damage to vesicles of importance in radiobiology has also been studied by the probe methods given above. Photoionization of solutes in vesicles has been observed for lecithin[188] and for synthetic vesicles.[189] The yield of photoionization increases with the optical clarity of the mixture.

The concepts of vesicle studies are readily carried over to membranes extracted from cells, to living cells,[81,84,190] and to proteins.[191-193]

Monolayers

Intriguing studies of photoinduced reactions have also been carried out in monolayers spread on water or taken up on slides. The results are of direct interest to vesicles and micelle studies, but as these systems are not colloidal and are not suspended in water or other solvents, space does not permit further discussion of these interesting systems. Excellent sources are available.[194-196]

J. Other Systems

There are many other examples of colloidal systems that act decisively in catalyzing both thermal and radiation-induced processes. Space only permits mentioning them in passing, although undoubtedly in the future they will play an ever increasing role in catalysis. Many mineral clays of the bentonite variety strongly promote chemical reaction.[197-199] These minerals can often be produced in finely divided form and act as genuine colloids in aqueous media. These particles possess SiONa groups, which ionize to give Na^+ ions and SiO^- groups on the particle. Neutralization of the SiO^- group leads to flocculation, and if this is carried out with cationic surfactants, then it is possible to produce a clay with a hydrophobic surface, which can be dispersed in organic media. The concepts used in micellar catalysis can be used with caution in these systems, bearing in mind the unique nature of the environment of the clay particle.

Several materials of immediate interest in storage of solar energy, such as semiconductors, can be dispersed in water by sonication, the solution achieving the unique photoelectron properties of the large solid-state systems. To date cadmium sulfide,[200] zinc oxide,[201] and silver chloride[203,204] have been shown to have photocatalytic properties when dispersed in aqueous media.

VI. Conclusion

The very nature of colloidal systems has, until recently, deterred photochemists from utilizing these microcosms in their studies. The complexity of the particles and the nature of their formation and structure appeared to raise too many complications to provide useful information in other simpler, yet still unknown, photosystems. However, modern physicochemical techniques and the sheer persistence of the colloid chemist can present convincing pictures of the many systems discussed here. In the meantime photochemists have established the photochemistry of many simple systems, and the sensitivity of spectroscopic techniques now available, especially laser methods, has improved by leaps and bounds in the last 10 years. The time is ripe for a wedding of these two fields of chemistry with rewards that are immediately recognized: the possibility of controlling and promoting photoreactions of interest. It is opportune that such research is coming into being right now, when it is most called for in the implementation of other systems for storage of solar energy.

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