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PHOTOCHEMICAL REACTIONS IN ORGANIZED ASSEMBLIES: ENVIRONMENTAL EFFECTS ON REACTIONS OCCURRING IN MICELLES, VESICLES, FILMS AND MULTILAYER ASSEMBLIES AND AT INTERFACES[1]

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INTRODUCTION

Surfactant or amphiphilic molecules having dissimilar hydrophobic and hydrophilic regions exhibit the important property of self-organization into a variety of molecular assemblies when they are exposed to environments ranging from non-polar to polar or mixed solvent systems. Some of these structures include monolayer films at an air-water or oil-water interface, vesicles which can range from ill-defined multilamellar structures to relatively well-characterized single walled, closed bilayer capsules having osmotic activity, various oil/water microemulsions and a wide range of loosely-organized assemblies classed generally as micelles. The driving force behind formation of many, if not all, of these assemblies is the so-called hydrophobic effect[2-4] which could be most simply defined as a tendency to minimize entropically unfavorable interactions and/or contact between molecules of markedly different polarity, e.g. hydrocarbon and water. While the properties of the various organized assemblies vary widely with structure of both the assembly and its component molecules, some of the most striking properties include the abilities of several assemblies to solubilize a wide variety of compounds to, in effect, produce extremely high local concentrations. In a number of cases charge and/or polarity effects can result in the media serving as a barrier inhibiting binding or penetration of various like-charged or polar reagents. In this report we will discuss a number of reactions—both thermal and photochemical—occurring in organized assemblies. This overview of work from our laboratories as well as a number of others will emphasize both the modification and in some cases control of reactivity which is possible through the use of organized media as well as the structural information that can be gleaned about the various media through our investigation of how these reactions are modified. This report will begin with a brief

overview of the structure and properties of the various organized assemblies employed as reaction media.

Micelles

Perhaps the most widely studied of all organized media both recently as well as in the past are micelles, usually formed by dispersal of single chain surfactants in aqueous solution. Early work in this area, commencing *ca.* 1913, was done by McBain, Hartley and others.[2,5] The most widely accepted model, originally developed largely by Hartley, presents a typical "small micelle" as consisting of a unit having several well-defined dissimilar phases. According to this model the roughly spherical micelle has a liquid-like hydrocarbon core from which water is excluded with the polar or charged head groups at the surface.[4,6] The surface is usually envisioned as being fairly rough such that the first methylene groups of the micelle are to some extent "wet."[6] A large fraction of the counterions (in the case of charged surfactants) reside in the aqueous layer immediately in contact with the head groups (Stern layer) and there is a diffuse double layer (Gouy–Chapman layer) surrounding this and extending up to several hundred Å which contains the remaining counterions. This "Hartley" model of the micelle (Fig. 1) has been widely used in interpreting many phenomena observed with micelles during recent studies.[7-9] As mentioned earlier the ability to solubilize a wide variety of substances to extremely high effective concentrations is one of the key properties of organized assemblies and this is particularly true of micelles. According to the above model one would predict that solubilization of solute molecules within a micelle could either occur inside the barrier imposed by the Stern-layer in the hydrocarbon "pool" for most nonpolar or slightly polar substances or in the surface region or Stern-layer for more polar or charged substances.[6,10] This simple picture, although used with apparent success in explaining numerous micellar properties and phenomena,[11-14] is complicated to some extent by the well-established dynamic properties of micelles. The lifetime of a single surfactant molecule within a micelle at room temperature is estimated to be in the range 1–100 μ sec.[15] The whole micelle is dynamic and rapid movement of solute within the micelle, perhaps between phases, is certainly to be expected.[15,16]

The Hartley model of the micelle has been challenged by a number of recent investigations using a wide variety of structural probes.[17-19] These studies in general suggest that the micelle structure is much more open and less organized than previously suggested. While the contrast between the classical Hartley model and more recently developed pictures will be discussed in more detail later on, a key feature of more recent structural models is the idea that many, if not all, solubilization phenomena involve location of the solute near the micellar surface or water–surfactant interface.[17-22]

The ability of micelles to solubilize and concentrate a number of dissimilar solutes has led to the occurrence of several reactions at accelerated rates compared to homogeneous solution, and in some cases even to the observation of reactions and/or products not otherwise obtainable.[7,23-28]

This has led to the proposal of micelles as a simple model for biomembranes and to several studies using micelles in the area of biomimetic chemistry.[24,26,27] While many interesting results have been obtained in these studies, present evidence concerning micellar structure as well as a careful evaluation of "true" intramicellar rates of reaction suggest that the analogy between micelles and the lipid portion of biomembranes or proteins cannot be carried too far.[25]

Swollen micelles and microemulsions

While simple micelles are usually formed as the result of mixing single hydrocarbon chain surfactants with water, a number of diverse microheterogeneous phases can result from admixture of hydrocarbons, alcohols, and/or other reagents to these components, depending upon the concentration domain involved.[29-37] Many of these structures are broadly classified as microemulsions, either oil-in-water or water-in-oil depending upon the proportion of water to hydrocarbon in the bulk mixture. While these

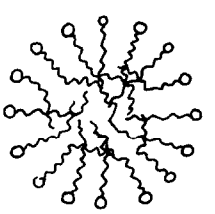


Fig. 1. Classical representation of a micelle (Hartley model).

structures in general have not been as extensively used or investigated as micelles, there has been much recent interest in their use as a perhaps superior and better-defined alternative to simple micellar media.[35,38–41] Admixture of nearly water–insoluble alcohols such as 1-hexanol or 1-heptanol to aqueous surfactant solution does not greatly increase the aggregation number of the surfactant; however since up to several molecules of alcohol per surfactant can be incorporated before turbidity occurs the aggregate should be much larger.[35] Although these aggregates could be classed as microemulsions, the term "swollen micelle" has been suggested as more appropriate to emphasize the close relationship between the alcohol-swollen and the conventional micelle[33] and will be used in this report. In contrast the structures formed from mixtures of surfactant, alcohol and hydrocarbon in water as the "solvent" can be regarded as true microemulsions consisting of reasonably well-defined (100–500 Å radius) droplets containing an "oil" core surrounded by a polar sheath of alcohol and surfactant interfacing with the water solvent (Fig. 2). Use of hydrocarbon as the bulk phase with small amounts of water incorporated results in formation of water/oil microemulsions or reversed micelles in which the "droplet" contains a small amount of water in contact with the polar head groups of the surfactants. This report will not deal with reactions in these water-deficient phases; the reader is referred to other reviews for a detailed discussion of their properties.[38,41]

Bilayer systems: vesicles and liposomes

Different kinds of assemblies from those discussed above are generally formed when surfactants containing two long hydrocarbon chains are dispersed in aqueous solution. In general these surfactants tend to form what are evidently more tightly organized structures ranging from multilamellar sheets to closed bilayer capsules variously referred to as liposomes or vesicles.[7,42–52] The types of surfactants forming the latter structures include natural surfactants such as the lecithins, cephalins or other phospholipids or synthetic materials such as dicetyl phosphate (DCP), dioctadecyldimethylammonium chloride (DODAC), or didodecyldimethylammonium bromide. In recent work a large number of vesicles formed from the synthetic surfactants has been characterized by several groups.[42,46–52] The closed single-walled bilayer vesicles formed by ultrasonic dispersion of DODAC or DCP are characterized by relatively high kinetic stability, a reasonably narrow size distribution (the structures are large enough to be characterized well by electron microscopy using freeze–fracture techniques), and osmotic activity.[42] In several cases these vesicles exhibit well-defined phase changes associated with "melting" of the hydrocarbon chains. The general reactivity and properties of these vesicles as well as liposomes (although there has been until now no clear standard as to the distinction between liposomes and vesicles, many authors use the former term when referring to structures formed from natural surfactants such as phosphatidyl choline and this report will follow suit) are in accord with a structure in which there is much more organization than in micelles or microemulsions with a very sharp phase boundary between the hydrophobic interior and the hydrophilic inner and outer faces. In general, permeability of the walls of vesicles or liposomes is restricted; modification of both the permeability and the apparent microviscosity can be obtained by addition of co-surfactants or other lipids such as cholesterol.

Recently a number of investigations have focused on the use of vesicles and liposomes for a wide variety of diverse applications ranging from selective delivery of drugs[53] to light-induced charge separation and energy storage.[42,47] The ability to selectively encapsulate reagents in the interiors (either at

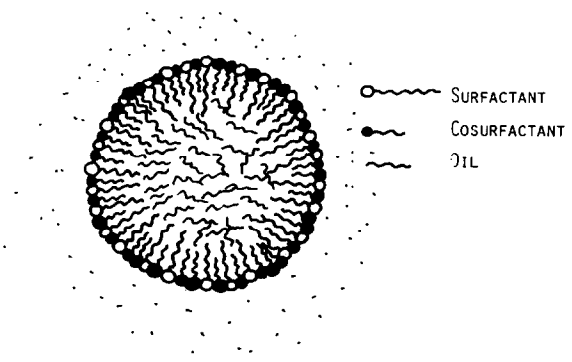


Fig. 2. Oil–water microemulsion.

the surface or the entrapped water pool) and to "exchange" or selectively modify the exterior environment offer numerous possibilities not available with micellar systems or most microemulsions.

Monolayer films and supported multilayer assemblies

The final two types of organized assemblies which will be discussed in this report are monolayer films, usually generated at an air–water interface but in fact possible to form in other environments (*vide infra*), and supported multilayers, usually formed by sequential transfer of these films from an air-water interface to a rigid support. The formation of films having thicknesses on the order of molecular dimensions has been recognized ever since the celebrated experiments of Benjamin Franklin with a teaspoonful of oil spread on the pond in Clapham Common.[54] Well characterized monomolecular films can be formed by spreading of water-insoluble surfactants from a volatile solvent at the air–water interface.[55] These films can be compressed in many cases to form highly condensed structures in which the polar or charged head groups interact with the surface water molecules, lowering the surface tension while the hydrocarbon residues are packed in a nearly crystalline array with the chains extended in a trans zig-zag arrangement close to that obtained in crystalline paraffins.[55–58] The films have proved useful in investigating molecular dimensions in a number of studies; as will be developed in this report, information gained by the study of functionalized surfactants in monolayer films can often be used in studies of the same molecules in other organized media.

While reactions and physical properties can often be investigated through studies of spread films at the air–water interface, assemblies that are, in principle, more interesting and more useful may be obtained by transfer of these films to rigid supports.[58–62] The techniques for preparation and study of these multilayer assemblies have been greatly improved during recent years and a variety of interesting applicaions of these assemblies have been developed.[55–58] The direct formation of monomolecular films on rigid supports via adsorption from solution has also been reported for many of the same surfactants forming films at the air-water interface; the adsorbed monolayers are relatively easy to prepare and the supported films exhibit properties similar to those obtained by transfer techniques.[63–66] The sequential buildup of multilayer assemblies using films of different composition offers many exciting possibilities for the construction of molecular arrays of known and controlled architecture. As with the other organized assemblies already discussed average separation between molecules is small such that local concentrations can be extremely high. The compressed films—to some extent—and the supported multilayers offer an additional feature in that the component molecules are often highly oriented compared to the other media previously discussed.[56] This offers additional possibilities for reaction control or restriction which are not possible in solution and certainly less likely in the more fluid assemblies.

Recent interest in interfacial reactivity, particularly in electrochemical phenomena, has resulted in a number of studies aimed at obtaining dense monolayer (or multilayer) coverage of reactive surfaces.[67] Multilayers formed from surfactants are potentially of use in these studies both with respect to possible film-surface interactions as well as interactions between molecules incorporated into the layer structure and solute or solvent molecules penetrating the assembly. Since multilayers formed from monolayer films are subject to relatively selective penetration by contacting solution reagents, several applications should be possible although thus far there has been no widespread use of Langmuir-type multilayers for these applications.

In the following sections we will discuss studies from this laboratory and elsewhere which review the role of the environment provided by these organized assemblies can play in controlling activity. The first section will focus mainly on structural information obtained by studies of reactivity—in this section the molecules used and their reactivity of properties thus can be viewed as probes of the specific microenvironment. The second section will deal with unusual reaction control or reactivity in organized assemblies and attempt to underline possible utility and practical applications of specific organized assemblies.

STRUCTURAL STUDIES OF ORGANIZED ASSEMBLIES USING REACTIVITY MODULATION AS A PROBE

Division in this Report of the discussion of reactivity in organized assemblies into two parts is rather arbitrary, since both parts focus on differences observed between the assemblies and more conventional homogeneous solutions and solids as reaction media. However the first section examines some cases where the phenomenon investigated occurs in both organized assemblies and conventional media but where sufficient modification of the rate or extent of a process can serve as a useful probe of the

microenvironment provided by the assembly or a specific rate therein. As is often the case in studies using probes, much of the information obtained is quite probe-dependent, indicating either that the probe can create its own microenvironment or that different probes reside in different and perhaps highly specific sites. Much of our work has focused on the selection of probes which should minimally perturb the structure of the organized assembly and reside in reasonably well-defined sites. A number of the probes synthesized and studied in our work are themselves functionalized surfactants which, being water insoluble, can reside only in the assembly. In several cases these molecules can be studied in films at the air–water interface such that the isotherms obtained provide structural information regarding their probable packing and orientation upon incorporation into surfactant assemblies.

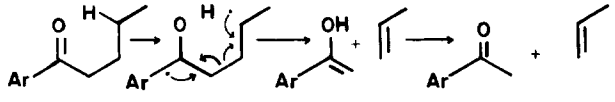
Surfactant aryl ketones in micelles and assemblies

Ketones undergo several photochemical reactions whose courses can be influenced by properties of the medium. These include both intra- and intermolecular hydrogen abstraction and the subsequent radical fragmentations and recombinations, and simple fragmentation at the carbonyl carbon. The first of these, the intramolecular Norrish Type II photoprocesses (Scheme 1) have been shown to be sensitive to the polarity of the medium.[68] In this reaction a γ hydrogen is abstracted by the oxygen of the excited carbonyl, creating a 1,4-diradical which may either fragment, ultimately to an olefin and a methyl ketone, or it may recombine to form cyclobutanol products. Hydrogen bonding of the hydroxyl of the diradical intermediate to the solvent stabilizes the hydrogen against back transfer, and in addition increases the apparent bulk of the hydroxyl, leading to a decrease in observed ratio of Z/E isomers of the cyclobutanol products formed.

Upon examination of the geometry of the type II reaction it becomes apparant that external steric as well as polarity effects may alter its course. Sometime during its excited state lifetime, the ketone must proceed through a six-membered transition state to reach the diradical intermediate. In micelles, which are characterized by rapid motion of the surfactant molecules this should occur readily; however in highly aligned systems such as bilayer vesicles below the phase transition temperature and supported multilayer assemblies, the twisting necessary to achieve this geometry would be disfavored, and less Type II cleavage would be the expected result.

Turro and coworkers used this solvent polarity dependency to determine the environment of the nonsurfactant ketones valerophenone and octanophenone in micelles of cetyltrimethylammonium chloride.[69] They compared the type II processes of these two water insoluble compounds in benzene, CTAC, and t-butanol (Table 1) and found results consistent with a highly polar environment for valerophenone and a moderately polar environment for octanophenone. They interpreted this to indicate a surface of Stern-layer position for the average site of solubilization of valerophenone in the micelle, and an average site somewhat further within the micelle for the more hydrophobic octanophenone.

Hartley and Guillet studied Type II cleavage in a 1% carbon monoxide in polyethylene copolymer in the solid phase from $-150°$ to $+90°$ (Table 2).[70] They found that at $-150°$ the reaction is totally suppressed, but increases to $\phi_{II} = 0.025$ at $-25°$ where it remains at all higher temperatures. They



Scheme 1.

Table 1. Type II cleavage and cyclobutanol product ratio of aryl ketones in homogeneous and cationic micellar media

medium	valerophenone		octanophenanone	
	ϕ_{II}	Z/E	ϕ_{II}	Z/E
tert-butanol	1.00	1.5	1.00	1.1
CTAC	1.06	1.9	0.71	1.2
benzene	0.33	3.6	0.29	4.7

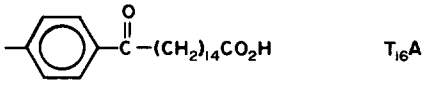
Table 2. Type II cleavage of ethylene carbon monoxide copolymer in solid phase

T °C	ϕ_{II}
90	0.025
24	0.025
-25	0.025
-50	0.015
-68	0.013
-95	0.005
-150	0.000

attributed this change in reactivity to a glass transition in polyethylene. Above $-30°$ there is thought to be free rotation about carbon-carbon bonds, at lower temperatures only cooperative motion of three or more carbons, and below $-120°$ no rotation whatever.

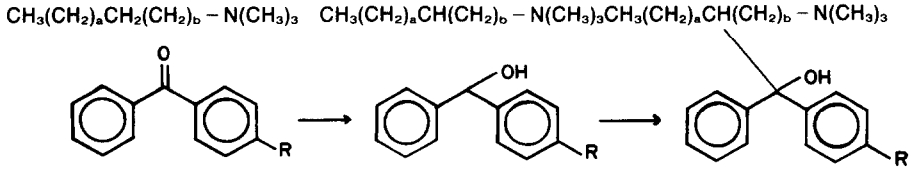
Intermolecular hydrogen abstraction has also been used to study the organization of surfactant media. Breslow has developed a series of surfactant benzophenone probes[71,72] which, when irradiated in surfactant assemblies, abstract hydrogen from a neighboring surfactant molecule to form a radical pair which then couples at the position of abstraction (Scheme 2).[71,72] The product is converted through a series of reactions to the thioketal, which can be quantitatively analyzed for the position of original hydrogen abstraction by mass spectrometry. When irradiated in either anionic or cationic micelles very little attack at the first four carbons of the surfactant was observed,[71] suggesting that the probe is oriented perpendicular to the micellar surface and that the carbonyl group is located in the micellar interior. Except for the terminal methyl, which was not attacked, the remainder of the carbons in the surfactant chain were attacked in a near random distribution, indicating considerable disorder in the micellar interior. Similar results were seen for vesicles of didodecylphosphate, however multilamellar dispersion of the same surfactant showed a significant preference for attack at intermediate carbons, located at positions near that expected for the benzophenone carbonyl in an aligned bilayer system.[72] Breslow took this to indicate a higher degree of order in the multilamellar dispersion than in micelles or vesicles, but cautioned that the high concentration of probe used (typically 1:2 probe:surfactant) may significantly perturb the structures of the systems investigated.

In our research into surfactant media we have emphasized the use of probes which minimize perturbation of the environment, and have focused attention on photochemical probes which are surfactants in themselves. One such probe, 16-oxo-16-p-tolylhexadecanoic acid, T16A,[73] is also capable



$T_{16}A$

of type II reaction. T16A behaves well as the surfactant; it dissolves readily in micellar solutions and, when mixed 1:1 with arachidic acid can be spread into monolayers at the water surface which are easily transferred to solid supports. Our results[74] for T16A and its shorter chain homolog, T10A, in homogeneous and micellar solutions parallel Turro's results for octanophenone: in benzene, $\phi_{II} = 0.20$; in SDS micelles, $\phi_{II} = 0.85$ for T16A and 0.87 for T10A. The high ϕ_{II} in micelles indicates that the ketone



Scheme 2.

experiences a polar environment; if the micelle is assumed to have the "Hartley" structure the ketone must be located in the surface region, whereas in a less structured micelle with considerable water penetration any solubilization site might be expected to have considerable polarity. Since the ketone is more polar than the aliphatic hydrocarbon chains of the surfactant molecules, it would be expected to seek a polar site, and so either explanation is plausible. In multilayer assemblies, on the other hand, much less type II cleavage product was detected. ϕ_{II} ranged from 0.058 in dry supported multilayer assemblies to 0.093 in assemblies saturated with pentane, while the quantum yield for disappearence of the ketone spectrum from the assembly increased from 0.134 to 0.148 as the reaction progressed from 0 to 30% completion. These results suggest that the steric requirements for type II reaction are easily met in micelles, but not in the more highly structured monolayer assemblies. Type II cleavage products are the only ones observed in solution and miceller media. In monolayer assemblies however only about half the product results from type II reaction, the remainder presumably resulting from intermolecular reactions with surrounding surfactant molecules. The increase in quantum yield for loss of ketone with reaction progress is not surprising. This most likely results from a "loosening" of the structure of the monolayer as reaction products leave the assembly.

Micelles and monolayer assemblies represent opposite extremes of a scale of medium organization which includes such intermediate examples as bilayer vesicles and microemulsions. We are currently using surfactant ketones with the same general structure as T16A to investigate bilayer vesicles, which might be expected to inhibit type II cleavage to a different extent above and below the phase transition temperature.

Photoisomerization as a probe for organized media

Photoisomerization about the olefin double bond has been intensively studied in solution media.[75-77] It is generally accepted that the excited state of either the cis of the trans isomer decays to a common twisted intermediate, "p", which then further decays to ground state cis or trans (Fig. 3). The ratio of trans to cis product in unhindered media depends primarily on the geometry of the twisted intermediate, though competitive decay processes such as fluorescence decrease the quantum yield of photoisomerization. Highly viscous media also decrease some photoisomerizations; the condition for a viscosity effect appears to be that the reaction must involve an increase in molecular volume. For stilbenes and many other olefins, the cis isomers of which are larger than the trans isomers, increasing the medium viscosity quenches only trans to cis photoisomerization; the cis to trans process, representing a decrease in molecular volume, is unaffected. In addition, the quantum yield for fluorescence of trans-stilbene increases with the viscosity induced suppression of photoisomerization, indicating that

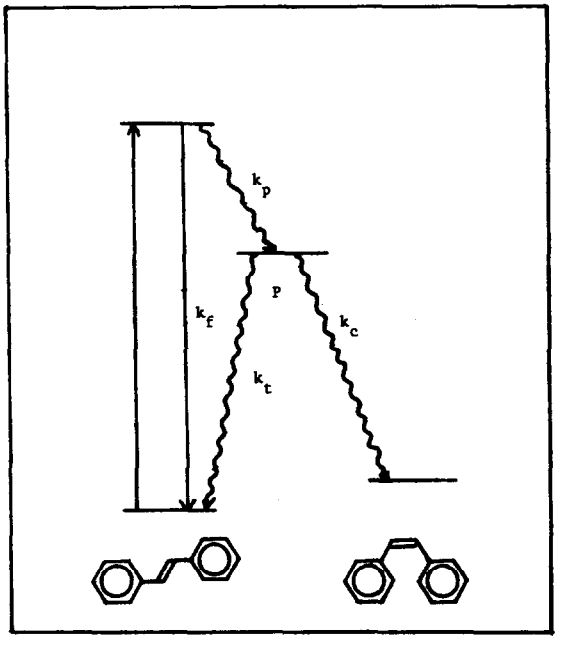
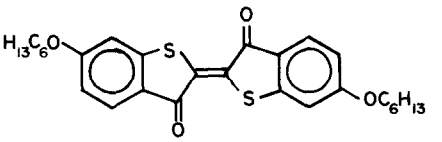


Fig. 3. Diagram of singlet state photoisomerization of stilbene.

even formation of the twisted intermediate is prevented. Evidently the solvent cage surrounding the trans stilbene molecule must be able to expand significantly during its excited state lifetime for isomerization to occur.

While the motion-restricting conditions which characterize most organized media are not appropriately refered to as viscosity, their effects on chemical reactions can be rationalized in a similar way. Trans–cis photoisomerizations of several olefins appear to be strongly affected by incorporation of reactants in organized media, the extent of the effect increasing with increasing organization of the medium.

An early study from these laboratories involved cis–trans photoisomerization of the thioindigo dye **1** in monolayers at the air–water interface, and in supported multilayer assemblies.[78] Reasonably pure solutions of trans or cis **1** could be obtained by irradiating a solution of the mixture to the photo-



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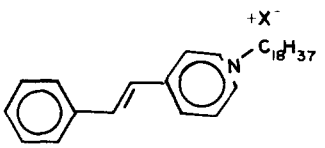
stationary state at 453 or 539 nm respectively. Multilayer assemblies of cis **1** were rapidly isomerized to trans by irradiation with visible light, however the trans isomer was photostable in the assembly. The same preference for the trans isomer was observed in monolayers at the water surface with the added feature that the surface area was reduced by 3% when a layer of cis **1** was irradiated with visible light. That the cis isomer requires more area at the water surface was confirmed by pressure-area studies of the pure isomers. These results suggest that, as in viscous homogeneous media, changes in molecular volume (or cross sectional area in this case) dictate the ultimate course of the reaction. Unfortunately, it proved impossible to transfer monolayers of cis or trans **1** to solid supports at low pressure. Irradiation of such assemblies might shed light on the pressure dependence of the direction of photoisomerization.

A surfactant derivative of 4-stilbazole, **2**, shows similar photoisomerization behavior.[79,80] In acetonitrile and CTAB micelles, irradiation at 366 nm results in establishment of a photostationary state containing about 70% cis. When this mixture is diluted with arachidic acid or tripalmitin, spread on the water surface and layered onto supports, irradiation returns it to the trans isomer. Monolayer assemblies of trans **2** cannot be converted to cis; rather, irradiation of such assemblies results in photodimerization



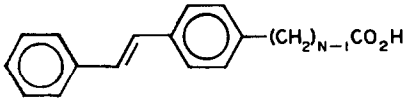
2

of trans **2** (*vide infra*). The ease of photoisomerization in both directions in micellar media shows that merely orienting the chromophore at a hydrophobic–hydrophilic interface does not restrict reactivity; the surrounding surfactant molecules in the monolayer assembly must exert sufficient lateral pressure to prevent the expansion necessary for trans to cis isomerization. When incorporated in a surfactant medium, the surfactant thioindigo, **1**, and stilbazole, **2**, are oriented with the chromophore in the hydrophilic portion, where reactions may be affected by the polarity of the aqueous phase and by interfacial effects. Results from the studies of these compounds suggest that the use of a more hydrophobic isomerizable olefin such as trans-stilbene might provide useful information about the hydrophobic region of a variety of organized assemblies. Trans-stilbene has several features which make it a desirable probe to investigate microenvironmental conditions. Its fluorescence and photoisomerization quantum yields have been shown to be sensitive to medium viscosity in the range expected in organized media;[76,77] it is hydrophobic and compatible in size and shape with the extended chain configuration of surrounding surfactant molecules; and its strong absorbance and fluorescence make it possible to use concentrations low enough to minimize probe-probe interactions as well as perturbation of the structure of the medium. The fluroescence and competing photoisomerization of stilbene have been extensively studied and the mechanism shown (Fig. 3) is generally accepted as correct. The excited trans-stilbene may either fluoresce outright (k_f) or it may twist to the "p" intermediate (k_p) which then decays either back to the trans or to the cis isomer with approximately the same likelihood. The

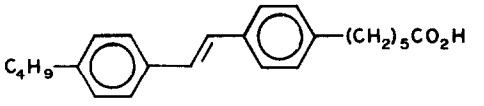
minimum activation energy for the twisting process has been determined to be about 2.7 kcal/mol.[77] In media with viscosities greater than about 10 cP this barrier is increased, increasing the fluorescence at the expense of photoisomerization.

Geiger and Turro used this viscosity dependence of fluorescence to study the membrane fluidity of vesicles composed of dipalmitoyl lecithin.[81] They observed a change in the temperature dependence of fluorescence when the temperature was increased beyond 41°, the phase transition temperature was increased beyond 41°, the phase transition temperature for DPL. A plot of $1/\phi_f - 1$ vs 1/T yielded activation energies of 4.2 kcal/mol above and 7.0 kcal/mol below Tc, that is, viscosity contributes significantly more to the activation energy in the gel phase below 41° than in the liquid crystalline phase above 41°.

Our laboratory has devoted considerable attention to the use of the stilbene chromophore in studies of several surfactant media.[82–84] We have prepared a series of surfactant probes S_N which contain the stilbene chromophore at various distances along a fatty acid chain. Whereas free trans-stilbene cannot



S_N N= 4,5,6,7, 10,12,16



$4S_6$

be localized within an assembly, the surfactant probe is anchored at the hydrophobic–hydrophilic interface by the acid group, the methylene chain presumably allowing the chromophore to extend a certain maximum distance into the assembly. In highly ordered systems such as bilayers and multilayer assemblies the fatty acid chain is expected to align with the surrounding surfactants, defining the exact distance of the chromophore from the interface and to some extent aiding in its alignment parallel to them. That this is the case is supported by the finding that monolayers of S_{16}, spread at the air–water interface, can be compressed to a limiting area of 20 Å^2/molecule, at which area the surface pressure increases sharply. This behavior is similar to that shown by other straight chain fatty acids. $4S_6$ also forms monolayers,[85] but compresses only to 24 Å^2, indicating that the stilbene moiety requires somewhat more space than a methylene chain, and that packing becomes more critical as the chromophore approaches the interface.

Both fluorescence and photoisomerization of S_{16} were shown to be strongly affected by incorporation into surfactant media (Table 3).[82] The quantum yield for fluorescence increased from 0.04 to 0.48 in going from methylene chloride solution to mixed anionic/cationic vesicles, while that for photoisomerization decreased from 0.50 to 0.14. In supported multilayer assemblies the quenching of photoisomerization was even more dramatic; the rigid order imposed by this system held the quantum yield for this process to a maximum of 0.0015. Similar high fluorescence yields have recently been observed for the shorter chain probes in vesicle solutions,[85] however their fluorescence quantum yields in micellar SDS have ranged around 0.12; in CTAC around 0.17. This suggests an SDS micelle considerably less organized than that produced by CTAC.

We have also used S_N in recent studies of vesicles, monitoring fluorescence as a function of temperature.[84,85] Like Turro we observe a distinct charge in temperature dependency of fluorescence at the phase transition (Fig. 4); however we observe phase transition behavior over a range of temperatures, with distinctly different behavior below and above this region. The plot of ϕ_f vs T is significantly steeper between 35° and 45° than either above or below, indicating a much sharper change in the organization of the hydrocarbon portion. This corresponds to an activation energy for reaching the twisted state of 6.6 kcal/mol below 35° C, and 5.3 kcal/mol above 50°; these values are rather close to each other, indicating little change in effective viscosity with temperature above and below Tc. The activation energy is 10.3 kcal/mol during the phase transition indicating that there must be a considerable change in viscosity in this region. This is the behavior expected in a gel to liquid crystalline phase transition. One possible reason for the difference between our results and Turro's may be the positioning of our surfactant probe at a specific distance into the assembly. Trans-stilbene is free to move to whatever part of the assembly favors it, presumably the parts with least restrictive organization. The

Table 3. Quantum yields for trans-cis photoisomerization and fluorescence of S_{16} in different media

medium	temp °C	$\phi_{t\to c}$	ϕ_f
CH_2Cl_2	22	0.50	0.04
CTAB[a]	22	0.39	0.18
DDAB[b]	22	0.38	0.23
	0	0.28	0.32
DCP/Lec[c]	22	0.38	0.23
	0	0.28	0.35
DDAB/DCP[d]	22	0.27	0.30
	0	0.14	0.48
ML[e]	22	$\leq$0.0015	-0.45

[a] Micelles composed of 0.05 M cetyltrimethylammonium bromide in water. [b] Vesicles composed of 0.05 M didodecyldimethylammonium bromide in water. [c] Mixed vesicles composed of 50:50 (molar ratio) dicetylphosphate:egg lecithin--total surfactant concentration 0.005 M. [d] Mixed vesicles composed of 50:50 (molar ratio) didodecyldimethylammonium bromide:dicetylphosphate--total surfactant concentration 0.005 M. [e] Supported multilayer assemblies of 1:1 S_{16}:arachidic acid.

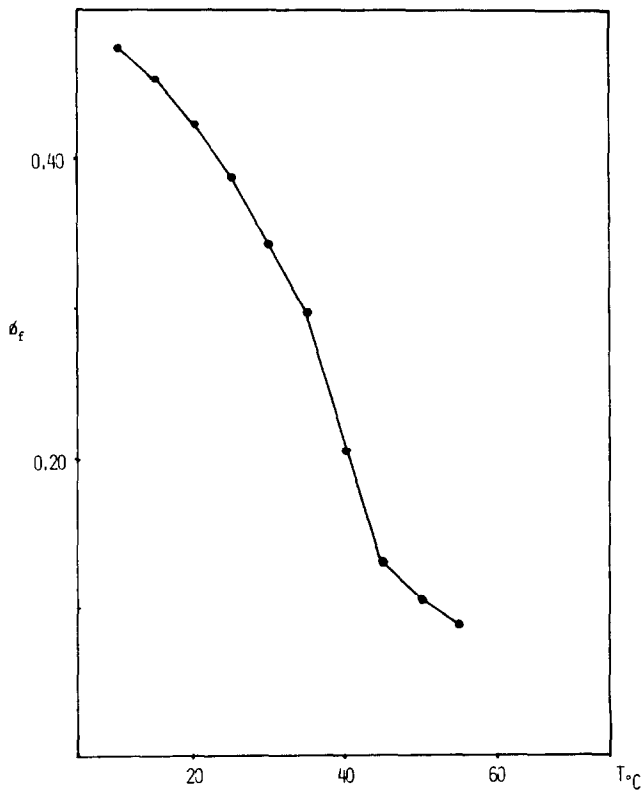


Fig. 4. Fluorescence quantum yield versus temperature of S_6 in vesicles of dipalmitoyl lecithin.

chromophore of S_N should be largely restricted to a position dictated by the length of its methylene chain.

Different behavior is observed in anionic vesicles composed of a mixture of dipalmitoyl lecithin and dicetylphosphate. The most striking difference is the much lower ϕ_f at lower temperatures (Fig. 5). Evidently the chromophore of S_6 sees a considerably less rigid environment in the anionic system; this may result from a mismatch in the hydrocarbon chain lengths of the surfactants (18 for DPL vs 16 for DCP) or, more likely, from a loosening of the system by the repulsion of the anionic DCP head groups. There is no literature value for Tc in this system, however a plot of ϕ_f vs T shows a change in slope at 40° indicating a change in viscosity dependence on temperature.

In addition to fluorescence and photoisomerization, the stilbene chromophore of S_N was found to form a weak nonfluorescent ground state complex with methyl viologen (Fig. 6),[83] effectively quenching its fluorescence. Anionic micelles, such as are formed from SDS, bind the cationic MV^{2+}, concentrating it with any other bound materials such as S_N. In a "Hartley" micelle the hydrophilic MV^{2+} would be expected

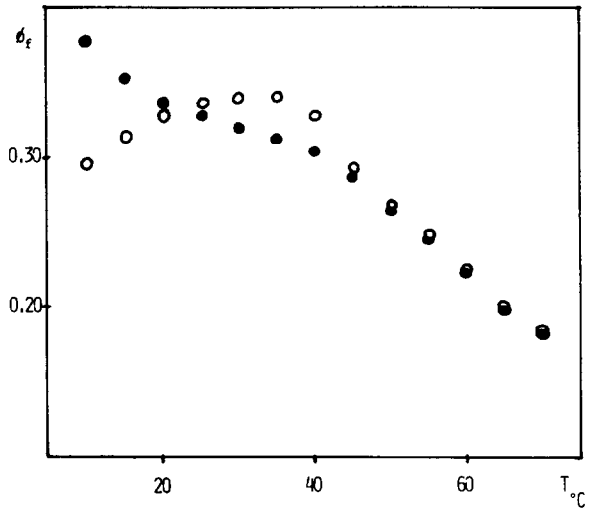


Fig. 5. Quantum yield for fluoroescence versus temperature of S_6 in vesicles of 50:50 dipalmitoyl lecithin; dicetylphosphate; O = with 1.5×10^{-3} M added methyl viologen; ● = without methyl viologen.

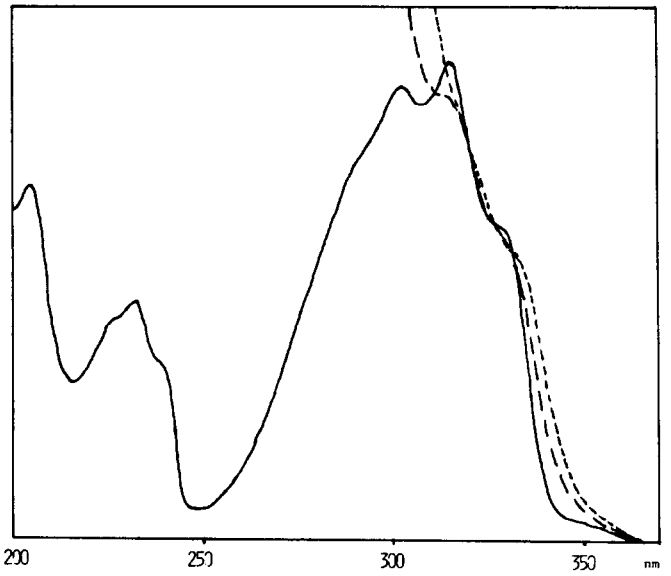


Fig. 6. Absorption spectrum of S_6 in 0.028 M SDS. ——, with no added MV^{2+}; ---, with 2×10^{-4} M added MV^{2+}; -----, with 1.5×10^{-3} M added MV^{2+}.

to reside in the surface region, the hydrophobic stilbene chromophore exclusively in the liquid-like hydrocarbon interior; the two should be brought together by the ionic and hydrophobic interactions of the micelle, but effectively held apart by their sites of binding. That this is not the case is shown by the uniformly high quenching constants (Table 4) found for trans-stilbene and all surfactant stilbenes with MV^{2+} in SDS micelles. The association constants, K_A, corrected for the concentrating effect of the micelle, are very similar to that for S_6 in acetonitrile, which suggests that the entire micelle may be available for the complexation process. These results support a much less organized structure for the SDS micelle than the Hartley model suggests; a highly open structure with little sequestering of inner from surface regions, and considerable hydrocarbon–water contact (Fig. 7). Ground state complexation between MV^{2+} and other such electron donors as 1-benzyl-1,4-dihydronicotinamide, 3-methylindole, and pyrene in SDS has also been observed by Verhoeven, whose results also support an open structure for the SDS micelle.

More recently the stilbene probes have been used to monitor properties of SDS micelles as a function of added cosurfactants. Intermediate chain alcohols such as n-hexanol and n-heptanol are throught to cause a "swelling" of the micelle structure;[87] the alkyl portion binds to the micelle by hydrophobic interactions while the polar neutral hydroxyl increases the separation of the ionic head groups of the surfactant, thus stabilizing the structure. This has been shown to lower the CMC and surfactant aggregation number N_A, and also to decrease the binding of counterions to the micelle.[88,89] Our results indicate that an additional effect is to induce a greater sequestering of inner from surface portions of the micelle, and to "tighten" its structure. Figure 8 shows K_A for several probes in SDS micelles plotted vs concentration of added heptanol. The association constant, corrected for the increase in volume of the

Table 4. Stern–Volmer and association constants for quenching of S_N flurorence by methyl viologen in SDS micelles at 20°

trans-stilbene derivative	K_{sv}	K_A
S_4	2150	14.5
S_5	2060	13.8
S_6	2440	16.4
S_7	2120	14.2
S_{10}	2250	12.6
S_{12}	1870	12.6
S_{16}	1020	6.9
trans-stilbene	2450	16.5

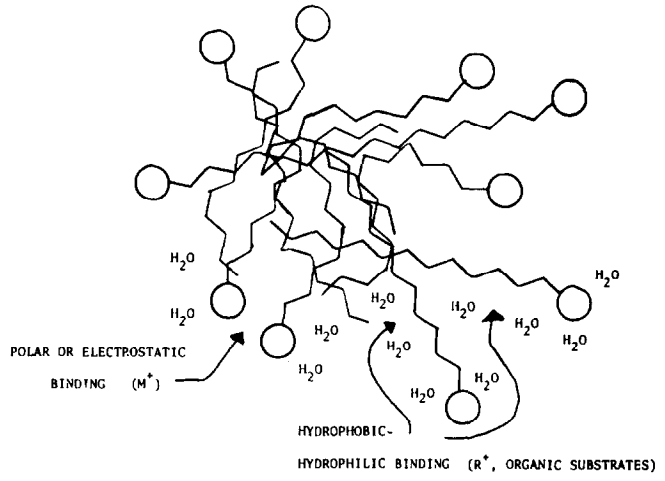


Fig. 7. Model for "open" structure of micelle.

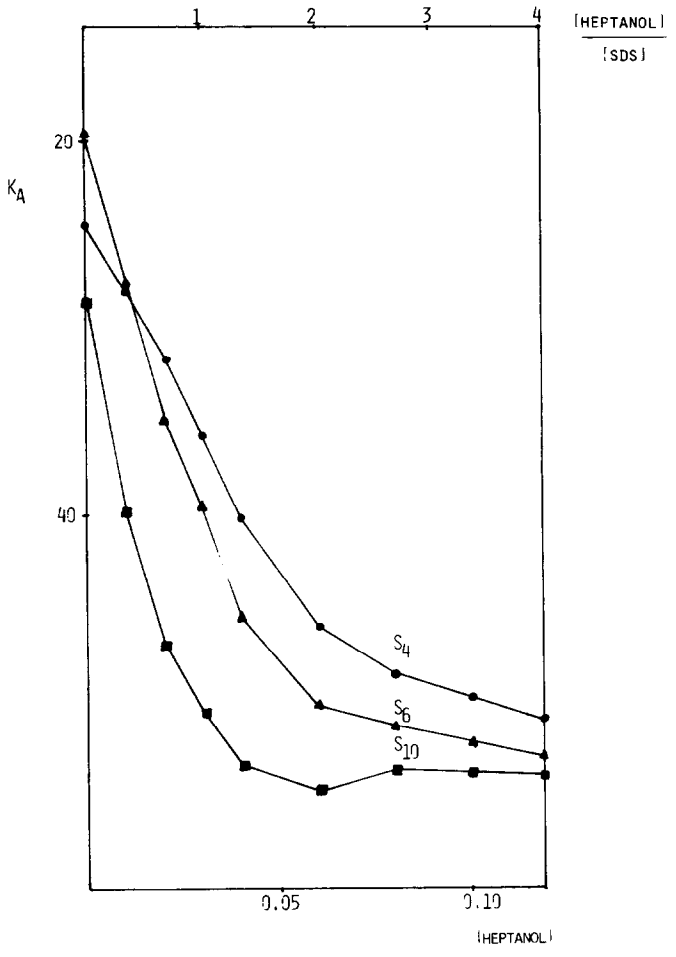


Fig. 8. Association constant vs. heptanol concentration for S_4, S_6, S_{10} in 0.03 M SDS at 20°.

hydrophobic portion, decreases rapidly at first, then levels out after the first two equivalents of heptanol indicating, perhaps, a change in micellar structure. Similarly, the fluorescence intensities of the probes increase significantly over the same range, indicating that the probe sees a greater effective viscosity in the swollen micelle.

Since the above-described DPL/DCP vesicle system is also anionic, MV^{2+} binds to it, and quenching of S_N fluorescence was studied as in SDS micelles (Fig. 5).[84] At low temperatures quenching does indeed occur, though the fluorescence intensity levels out well above zero, indicating that some of the stilbene chromophore is held away from the vesicle surface presumably through alignment with the hydrocarbon chains of the surrounding surfactants. At temperatures near the apparent phase transition the addition of MV^{2+} actually increases the fluorescence of S_6, presumably by neutralizing the repulsive interactions between the anionic head groups of the surfactants, allowing the system to become tighter, and more "viscous" to the chromophore. Above the phase transition MV^{2+} has little effect, indicating that here the hydrocarbon chains of the surfactants are too fluid for changes in head group interactions to be felt by the stilbene.

The stilbene probes S_N were designed to study the microenvironment in hydrophobic portions of surfactant assemblies; they also appear useful in studying the relationship between hydrophobic and hydrophilic portions. Micelles, rather than sequestering hydrophobic reagents like monks in medieval monasteries are shown to leave them open to external influences. Only vesicles, those stalwart fortresses of ancient legend, and capable of protecting their innocence and even so only at high temperatures.

Excimer formation as an organized media probe

While our group has concentrated on reactions (fluorescence, photoisomerization, complexation) of the stilbene chromophore as a probe into microenvironmental conditions in organized media, other

groups have devoted considerable study to intra and intermolecular excimer formation of several surfactant and nonsurfactant compounds. Excimer formation of the pyrene chromophore has been used to investigate several surfactant systems including micelles, vesicles and monolayers. The probes have included pyrene itself,[90,91] 1, 3-di(1-pyrenyl)propane,[92,93] pyrene at the end of a long chain fatty acid, and pyrene lecithin (1-palmitoyl-2-pyrenedecanoyl phosphatidyl choline).[94] They have been primarily used to study diffusion characteristics and microfluidity of bilayer systems and micelles, though they have also been useful in studying aggregation phenomena in monolayers.

When electronically excited by absorption of a photon, pyrene may either fluoresce outright, or it may associate with a second ground state pyrene in an attractive interaction and then fluoresce with a spectrum characterized by longer wavelengths and no vibrational structure. The relative amounts of monomer and excimer fluorescence depend on the concentration of pyrene and the viscosity of the medium. Because of anisotropy and short range inhomogeneity in organized media the concept of viscosity is of doubtful value, however its units do provide a convenient, intuitively satisfying measure of the rapidity with which molecules can diffuse, and a number of studies have reported values for microviscosity based on comparisons between reactions in organized and homogeneous media.

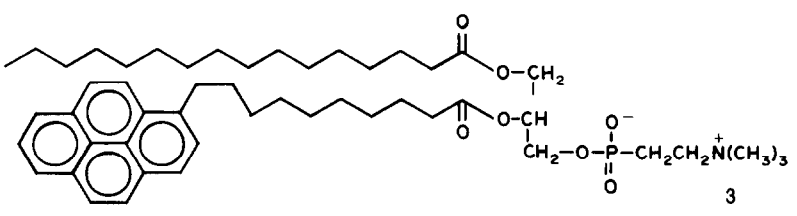
In one such study, Pownall and Smith investigated C10, C12, C14, C16–TAB, C18–TAC, sodium deconate, and SDS micelles.[90] They measured the ratio of excimer to monomer fluorescence, I′/I, of pyrene in a series of solvents of varying viscosity to determine the viscosity dependence, then formed I′/I for the same effective concentration (corrected for the concentrating effect of the micelles) in the various surfactants. They obtained values of 130–155 cP for the cationic micelles, 150 cP for sodium decanoate, and 193 cP for SDS.

The use of intermolecular excimer formation as a microviscosity probe requires doubly occupied micelles; results are complicated by the presence of singly occupied micelles and micelles containing more than two probe molecules. To obtain enough doubly-occupied micelles to make useful spectra it is necessary to use relatively large concentrations of probe, which increases the fraction of micelles containing more than two probe molecules. This may significantly affect the structure of the micelles. Several groups avoided this problem by using probes which form[92,95,96] intramolecular excimers. Such probes provide the necessary "double occupation" at very low concentrations, minimizing perturbation of the system. Zachariasse obtained the much lower value of 19 cP for the microviscosity of SDS using 1, 3-di(1-pyrenyl)propane.[92] Other groups using similar 1, 3-diaryl propanes found values around 10 cP for SDS, 20 cP for C16TAC and 40 cP for C16TAB.[95,96]

Zachariasse has used the same probe to study microfluidity in vesicles and bilayers of dimyristoyl and dipalmitoyl phosphatidylcholine as a function of temperature.[93] Plots of I′/I vs temperature show the expected behavior: very little excimer fluorescence below Tc, a sharp increase at Tc, and a steady increase above. The microviscosity of dimyristoyl lecithin in the gel phase was determined to be 125 cP while that in the liquid crystalline phase was 38 cP. The corresponding values for dipalmitoyl lecithin were measured at 30 and 18 cP respectively. Broader phase transitions were observed in sonicated vesicles than in the bilayers; presumably the high surface curvature decreases the order of the system below Tc, decreasing the cooperativity of the phase transition.[93]

Galla and Sackmann measured the ratio of excimer to monomer fluorescence I′/I of pyrene in dipalmitoyl lecithin bilayers as a function of temperature and cholesterol content to determine the rate at which it can diffuse in the bilayer.[91] They found that above the phase transition increasing the temperature increases I′/I, indicating a higher rate of diffusion. Below Tc the pyrene appeared to aggregate in the ground state, resulting in more excimer formation than expected. Cholesterol decreased I′/I at all temperatures indicating that its presence decreases membrane fluidity, an observation supported by spin label studies.

Galla *et al.* also developed the probe pyrene lecithin, **3**, which is similar enough to the usual



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phospholipid surfactants that it is expected to have similar diffusional characteristics. Using a treatment

similar to that for their pyrene work they found values of 1.7×10^{-7} and 0.77×10^{-1} cm^2/sec for lateral diffusion coefficients in dipalmitoyllecithin at 60°, very close to the value obtained from similarly designed spin probes. Phospholipid exchange between vesicles and from inside to outside layers of vesicles could also be measured by mixing pyrene lecithin doped vesicles with undoped vesicles and observing the rate at which I'/I decreases. Two reaction processes were observed, one very fast and one much slower. In the first the ratio I'/I decreases to 75% of its original value with a half life of 11 sec corresponding, the authors suggest, to exchange of surfactant between the outer layers of doped and undoped vesicles. This is somewhat surprising, since vesicles are thought (and demonstrated) to be stable for long periods of time, typically weeks. Presumably these uncharged vesicles may contact each other, exchanging surfactant without actually coalescing, though the possibility should not be ruled out that the pyrene chromophore somehow aids this process for the labeled surfactant. In the second relaxation process I'/I decreased to about 50% its original value with a half life of 8 h, corresponding to exchange of surfactant between the inner and outer surfaces. It appears from this that head group interactions between vesicles favor exchange, but when the head groups are separated by the hydrophobic portion of the bilayer, exchange is strongly inhibited.[94]

In many ways the stilbene and pyrene probes are complementary. The pyrene chromophore, because of its intermolecular excimer formation, is useful in measurement of diffusion within and between vesicles. The intramolecular excimer forming probes provide a convenient means of comparing microviscosities of several organized media. The stilbene probes yield information on microviscosity as well as the relationship between hydrophobic and hydrophilic regions of surfactant assemblies. While results from the studies of fluorescence of S_N have not been translated to units of viscosity, they appear to aggree well with those obtained from the 1,3-diarylpropane excimer studies, showing microviscosity to increase in the order SDS < CTAC < bilayer vesicles. The surfactant stilbenes have the advantage that they can be located with some degree of confidence at a depth within the lipid bilayer determined by the alkyl chain length. This is indicated by differences in plots of ϕ_f vs T between homologs of S_N in vesicle systems.[85] The diarylpropanes on the other hand have the advantage of being useful in systems which are not transparent, such as multilamellar structures, since it is the ratio of excimer to monomer fluorescence, I'/I, rather than the quantum yield of fluorescence which is measured.

Counterion effects on micelle structure

The structure of any surfactant will necessarily depend upon the environment in which the aggregate exists. Since this review deals primarily with surfactants in aqueous solutions, an important consideration involves the effects of added salts on the structure and properties of the aggretates. A large body of literature exists describing effects of added salts on micellar properties such as the CMC, aggregation number, and degree of dissociation of the charged head groups of ionic micelles.[22,97-102] Previous studies have shown that the micelle size and CMC are affected strongly by varying the specific counterion employed.[22,97,100] For instance, the CMC decreases and the aggregation number increases as the counterion of dodecyl sulfate is changed from lithium to cesium in the alkali metal series.[22] A decrease in the hydrated radius of the counterion employed results in an increased electrostatic shielding of the anionic head group (tighter ion pairing), thus lowering the CMC. However the opposite trend is observed with tetraalkylammonium ions, where hydrophobic stabilization of larger alkylammonium ions within the micelle brings about dramatic decreases in the CMC and corresponding increases in aggregation number.

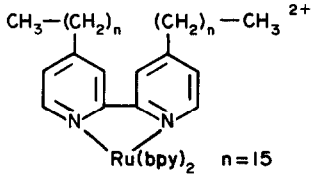
Further, micellar properties are markedly affected by the concentration of added counterion. Increases in ionic strength result in decreases in the CMC and increases in micelle size.[12,103,104] Eventually a point is reached in which the shape of the micelle also changes and large multilamellar aggregates begin to form.[104]

The examination of chemical reactions in micelles involving one or more charged reactants can provide information regarding micelle structure and properties not readily available by classical physical methods typically used to determine CMC's, aggregation numbers, and micelle shapes. For example, recent work done in our and other laboratories[105-110] provides a description of ion-exchange phenomena between aqueous and micellar phases as shown below. The subscripts aq and mic refer to

$$S^+_{mic} + Q^+_{aq} \rightleftharpoons S^+_{aq} + Q^+_{mic}$$

aqueous and micellar phases respectively, S^+ is the micellar counterion (for an anionic detergent) and Q^+

represents the added charged reactant. In our work a small fraction of the micelles are doped with a chromophore that can be easily oxidized upon electronic excitation and, choosing a weak oxidant as Q^+, one may examine the above ion-exchange process by probing the excited state electron transfer reaction (see Scheme 3). We examined the emission quenching of a surfactant ruthenium complex, **4**, by the dicationic electron acceptor N, N'-dimethyl-4, 4'-bipyridinium (methyl viologen) in the presence of SDS micelles. The degree of emission quenching of **4** decreases with (1) increasing surfactant concentration



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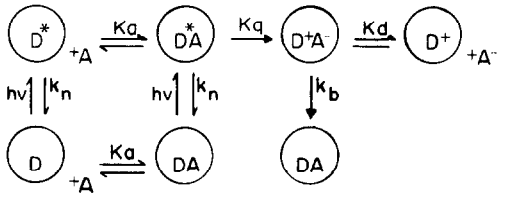
and (2) increasing salt concentration. Examination of the emission decay of excited **4** in the presence of quencher established that the bipyridinium dications exchanged between micelles very rapidly and, as a result each excited ruthenium complex encounters the average number of quenchers bound to the micelle during the excited state lifetime of the complex. From analysis of the quenching as a function of ionic strength an estimate of the ion exchange equilibrium constant (eqn 1) was obtained. Table 5 lists ion-exchange constants determined for a number of dodecyl sulfate salts with the bipyridinium salt. Comparison of the values provides a measure of the relative affinity of the counterions for the sulfate head groups of the surfactant: $Li^+ < Na^+ < NH_4^+ < (C_2H_5)_4N^+ < Mg^{2+}$. The results parallel values obtained for CMC's and heats of formation[111] for the series of dodecyl sulfates. The ordering of affinities of the ions reflects the importance of both electrostatic and hydrophilic–hydrophobic interactions in influencing association of counterions with surfactant micelles. Generally the association of the counterion with the micelle increases with increasing charge density and with increasing hydrophobicity of the counterion. This order is close to that for the "lyotropic series."

Another aspect of counterion interaction with surfactants important to micelle structure is the degree of dissociation of counterions with the micelle. The fraction of ionized head groups of the aggregate is an important consideration in examination of the dynamics of reactions involving one or more charged reactants. Several reports of ion saturation of micelles have appeared in the literature recently.[112–116] The



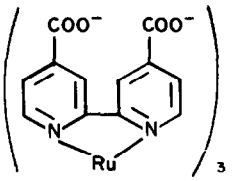
Scheme 3.

Table 5. Exchange equilibrium constants and Stern–Volmer constants obtained for quenching of **4** by methyl viologen

salt	k_{ex}	$k_{sv} M^{-1} s^{-1}$
NH_4Cl	5625	1587
LiCl	3566	2061
$MgCl_2$	102	2237
NaCl	868	3155
TEAC	279	9259

previous results have involved principally the examination of association of metal ions with micelles and have emphasized the importance of electrostatic interactions.

The limiting association of the methyl viologen dication, N, N'benzyl viologen and copper(II) ions with SDS micelles has been determined in our laboratory by examining the quenching of the tetraanionic ruthenium bipyridyl complex, **5**, by the above cations in the presence and absence of SDS.[117] Figure 9



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shows a plot of the degree of quenching as a function of the quencher concentrations when the dimethyl bipyridinium cation is the quencher. At low quencher concentrations the surfactant/quencher ratio is large and the cationic bipyridinium is principally associated with the anionic micelle. The anionic ruthenium complex, **5**, is repelled from the micelle and, as a result, very little quenching occurs. As the quencher concentration increases the micelles present in solution become saturated, and above the saturation point, very efficient quenching of **5** occurs in the aqueous phase. Results from this type of investigation reveal that the micelle accomodates one copper ion for every six surfactants, one methyl viologen for every 3.4 surfactants and a single benzyl viologen for every 2 to 3 surfactant head groups. The values are opposed to those expected assuming electrostatic interactions predominate for the association of the three ions with SDS. The result for the copper Cu(II) ion is similar to a value obtained by an independent method [114] and it is unlikely that effects other than electrostatic interaction influence the association with dodecyl sulfate micelles. The dimethyl- and dibenzyl viologen ions have a much more diffuse charge distribution than Cu(II); these large planar organic ions probably associate with the micelle via hydrophobic- hydrophilic interactions and the degree of association is related to the number of hydrophobic- hydrophilic interface sites available for binding.

Evidence that hydrophobic effects play a major role in the binding of organic cations comes from a comparison of the monocations 4-cyano-N-methylpyridinium (CMP^+) and 4-cyano-N-benzylpyridinium (CBP^+). Both of these ions quench the luminescence of the tetraanionic ruthenium complex **5** in aqueous

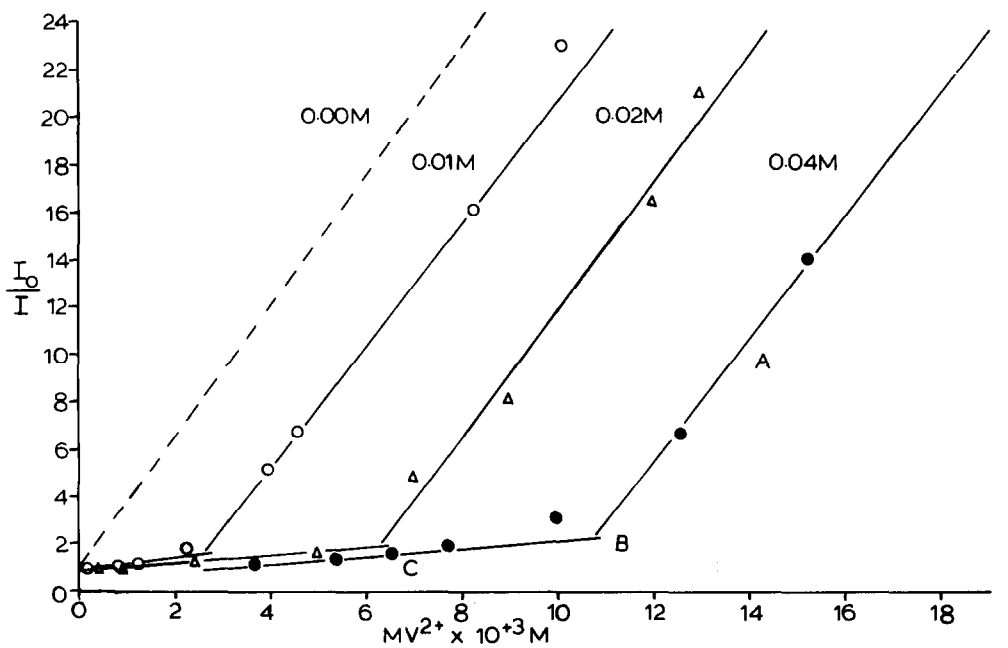


Fig. 9. Quenching of **5** by methyl viologen as a function of the SDS concentration.

solutions. Addition of SDS above the CMC attenuates the quenching of both CMP^+, and CBP^+.[117] The quenching of CMP^+, which is quite water soluble, shows a different effect from that obtained for dimethyl and dibenzyl viologens suggesting that CMP^+ simply partitions between aqueous and micellar phases. In contrast the much more hydrophobic CBP^+ shows attenuation similar to that observed with the viologens; however the limiting capacity of the micelle for CBP^+ is even greater (1CBP^+/two surfactants) even though coulombic attraction for this ion should be much lower.

The binding of viologen and related organic cations to other surfactants has been studied by the same technique; here again the results suggest the role of hydrophobic–hydrophilic interactions. Thus we find that increase in the length of the hydrocarbon chain in the series sodium decyl sulfate, sodium dodecyl sulfate, sodium tetradecyl sulfate and sodium hexadecyl sulfate results in an increase in the number of viologen cations bound/surfactant molecule in the micellar phase. These results, together with those cited earlier for the stilbene–viologen complex, suggest once again that the structure of simple micelles is quite open as indicated in Fig. 7 and that appreciable hydrocarbon–water contacts exist at any time. The elimination of these contacts by insertion of moderately polar reagents such as these organic cations provides a strong driving force for solubilization; the interfacial binding occurring is fairly unique and not easily modeled by available homogeneous solutions.

Such a picture of ion association of micelles suggests that some penetration of the aggregate by the ion takes place to aid in stabilization of the association complex. Very little information is available describing ion penetration of micelles as definitive experimental results are difficult to obtain. Most observations of ion penetration of surfactant organizates have involved vesicles and black lipid membranes.[118–121] Recent evidence in our laboratory[83] suggests that micelle penetration by reasonably large organic ions may indeed be quite facile given favorable electrostatic situation (i.e. cationic ion with anionic micelle). We observed that the methylviologen ion forms a ground state complex with a number of surfactant stilbenes, as discussed in the previous section. The complex forms even when the stilbene is encapsulated within SDS micelles. Further, the association constant varies only by a factor of 2.5 upon increasing the hydrocarbon chain length of the stilbene from four to sixteen (see Table 4). The longer chain stilbenes occupy sites further removed from the surface of the micelle and as a result the association constant decreases somewhat. The rather small decrease observed suggests that the micelle does not sequester the surfactant stilbenes from the polar methyl viologen, indicating that penetration of the micelle by the cationic viologen is facile. This observation is of interest as more rigid surfactant aggregates such as vesicles and liposomes have been shown to be relatively impermeable to organic ions. Fendler has observed that dihexadecyl phosphate vesicles are capable of trapping methyl viologen

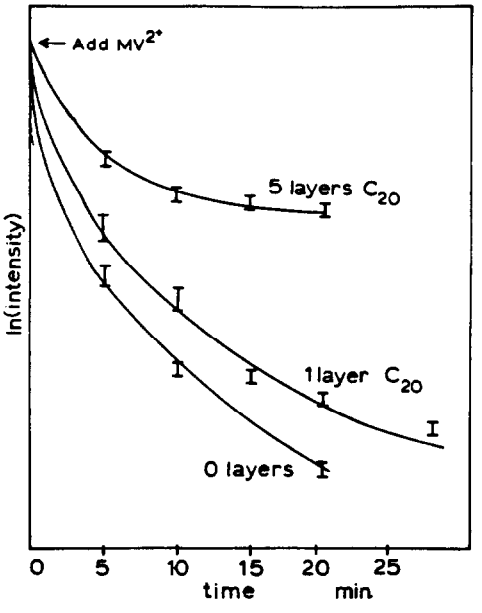
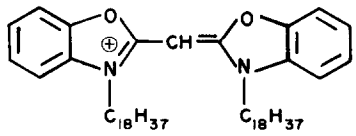


Fig. 10. Decay of emission of a single monolayer of **6** with 0, 1 and 5 insulating layers of cadmium arachidate at several times after addition of MV^{2+} (0.005 M).

cations in the inner surface for prolonged periods.[47] Examination of the stilbene–viologen systems in dicetylphosphate vesicles demonstrates the temperature dependence of such permeation[84] (see previous section).

Multilayer assemblies of fatty acids, such as arachidic acid, doped with small amounts of probe surfactants have also been used to examine ion penetration effects. In such cases permeation of the built-up assemblies by ions in solution is dependent upon a variety of factors, including imperfections in the films and adsorption of ions through channels created at the edges of the solid support. Nonetheless, the effects of insulating a probe molecule within an assembly from ions or other solutes may be approached; however, no absolute comparison of the permeabilities of these assemblies with the other aggregates discussed above is possible. As with vesicles, such penetration is of interest in defining characteristics of ion diffusion through biological membranes. Penetration of assemblies by neutral solutes was addressed by Kuhn.[66] Penetration of films containing a surfactant diazonium salt by 8-hydroxyquinoline to yield azo dyes established that the solute did not disrupt the film structure. The same films were also found to be penetrable by a cationic thiocyanine dye.[66] We have examined penetration of assemblies of arachidic acid containing surfactant porphyrins (vide infra) by metal ions.[122] By monitoring the rate of porphyrin metalation we were able to determine the effect of protecting outer porphyrin layers by covering them with insulating layers of arachidic acid. Covering the exposed films with a single layer of arachidic acid resulted in a decrease of the porphyrin metalation rate of 20%. Upon depositing a second layer the rate decreased to 25% of the original (75% reduction). Addition of further layers resulted in no further decrease in the metalation rate. The lower limiting rate reflects ion penetration through edge imperfections of the solid support. Addition of a single layer results in a film with imperfections allowing rapid ion penetration; upon addition of the second insulating layer no metalation occurs as a result of direct penetration of the film. Thus, as with vesicles, it appears that monolayer assemblies form highly impenetrable bilayer units; in these assemblies the bilayers are stacked to form the assembly. Similar results were obtained in examining the emission quenching of an oxocyanine dye by methyl viologen, Cu(II), and iron (III) ions.[123] When the dye 6 is incorporated into the



6

outer layer of a lattice of cadmium arachidate, the emission of the dye can be observed upon ultraviolet excitation. Upon adding methyl viologen as quencher, the emission gradually decreases (Fig. 10) over a 30 min period before plateauing. The emission can be partially regenerated by addition of nonquenching cadmium(II) ions to the aqueous phase. Figure 10 also demonstrates the effect of insulating the layer containing **6** with successive layers of cadmium arachidate. Little change in the quenching is observed upon addition of a single insulating layer; however, a dramatic decrease in the quenching occurs upon covering the emitting layer with five layers of the host surfactant. Thus, as with the porphyrin metalation, protecting the reactive portion of the film by adding successive bilayers greatly inhibits ion penetration. Further, it appears that ion-exchange equilibria also play a role in influencing ion penetration of the assemblies.

The foregoing results present a widely varying picture of the degree of organization of the different assemblies studied ranging from simple micelles, which are dynamic and probably highly disorganized, to the multilayers which are static and quite regular, perhaps almost crystalline in structure. The "swollen micelles", oil/water microemulsions and vesicles examined in these investigations clearly appear intermediate in structure with some relatively clear demarcation of hydrophilic and hydrophobic regions and a corresponding phase barrier. However some roughness and disorder persists in these media resulting in the possibility of solubilization via hydrophobic–hydrophilic interactions similar to those occuring in micelles. A key result from the studies using different probes is the finding that the degree of organization in micelles and presumably the other organized assemblies formed in aqueous solution, can be modulated by the addition of co-surfactants or other reagents in a reasonably systematic manner.

CONTROL AND/OR MODIFICATION OF REACTIVITY IN ORGANIZED ASSEMBLIES

The foregoing discussion of structural studies of organized media included several cases where the normal pattern of solution reactivity was altered either by the slowing down of some processes or the effective acceleration of others. Thus the "normal" photoreaction paths of ketones and olefins are hindered in certain media while other processes such as ground-state complex formation between stilbene and methyl viologen can be rendered more favorable. The major consequences expected to modify chemical reactivity in organized media would be anticipated to include enhanced or selected solubility resulting in unusual concentration effects; specific orientation effects in some media, restrictions of molecular motion, and special hydrophobic, hydrophilic or charge effects. In the last section of this review we examine several cases where one or more of these effects produce overall reactivity in various assemblies substantially different from that observed in solution. The examples discussed are by no means exhaustive but they serve to indicate the wide range of possibilities that exist with different types of reactants in various assemblies.

Metallation of porphyrins organized assemblies

Chelation of neutral organic ligands by transition metal salts frequently is hindered by problems associated with the solubilization of both the ions and the hydrophobic ligand. Because of this solubility incompatibility such reactions provide an excellent opportunity to probe the role of surfactants in affecting the rate of reactivity of a water insoluble ligand with a metal ion. As well as obvious electrostatic interactions between the metal ion and the surfactant aggregate, the chelation process may be affected by the specific orientation of the ligand within the organizate. Kinetic studies of chelation of pyridine-2-azo-p-dimethylaniline by Ni(II) and Zn(II) have demonstrated that rate enhancement occurs in the presence of sodium dodecyl sulfate (SDS) micelles via concentration of the reactants at the micelle–water interface.[124, 125] Theoretical descriptions of the distribution of metal ions around spherical colloidal particles employing non-linearized Poisson–Boltzman equations have been presented by a number of investigators.[116, 126–129] Double layer potentials on the order of 150 mv have been determined.

The metallation of free base porphyrins has been extensively examined in micelles, microemulsions and monolayer assemblies. The effects of addition of phase transfer catalysts and alterations in the porphyrin structure have been examined. Phillips and Lowe[130] explored the insertion of Cu(II) into protophyrin dimethyl ester in the presence of SDS and CTAC micelles. It was observed that the addition of weakly chelating molecules expected to be solubilized at the micelle–water interface greatly accelerated the metallation process. Table 6 presents the relative rates of metallation as a function of the added phase transfer catalyst. The authors also observed that the metalation process was completely halted when the porphyrin was solubilized within cationic micelles.

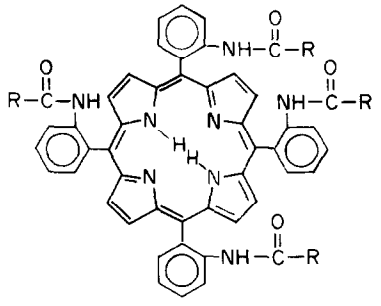
Similar effects were observed by Letts and Mackay for Cu(II) insertion into tetraphenylporphyrin in the presence of oil in water microemulsions composed of benzene water, cyclohexanol and sodium cetyl sulfate.[39, 40] A series of added cofactors were observed to strongly influence the metallation. For example, addition of 2, 2-bipyridine or ethylenediamine completely blocks the reaction by competitive chelation. As in micelles a sizeable acceleration (factor of 1000) is observed in the presence of quinoline. The interface region of the microemulsion also provides an environment which stabilizes several

Table 6. Effect of cofactors on metallation rate of proto-IX-DME in SDS micelles

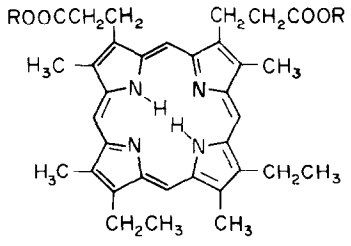
cofactor	rel. metallation rate
sodium diethyldithiocarbamate	1650
2-hydroxypyridine-N-oxide	500
8-hydroxyquinoline	375
salicylaldehyde	55
no cofactor	10
glycine	5
2,2'-bipyridyl	2.5
EDTA	1

intermediates in the porphyrin metalation process in the presence of triphenylphosphine.[40] Several Cu(II)-triphenylphosphine–porphyrin complexes were isolated and characterized. The rate relative to solution metalation varies as a function of (a) the extent of association of the metal with the cofactor and (b) the ability of the cofactor to act as a Bronsted base in removing protons from the porphyrin core.

Examination of these processes in monolayer assemblies[122, 134] focused on altering the solubilization site of the porphyrin rather than influencing the mode of transport of the metal ion into the lipophilic portion of the assembly. The insertion of Cu(II) into a series of related porphyrins was monitored in solution, monolayer films at an air–water interface and in monolayer assemblies. The porphyrins examined were amides of tetra(o-aminophenyl)porphyrin (shown below) first synthesized by Collman[133] and mesoporphyrin-IX-dioctadecylester, containing only two hydrophobic chains.



7: R = methyl
8: R = t-Butyl
9: R = hexyl
10: R = hexadecyl



11: R = octadecyl

Absorption spectra of the various amides as assemblies built up from phosphate subphases demonstrates no evidence of interporphyrin interactions. A lack of such interaction implies that the porphyrin plane is parallel to the plane of the interlayer interface. The visible absorption spectrum of the mesoporphyrin derivative revealed dimer formation.[135] Surface pressure-area isotherms of the porphyrins gave areas at constant pressures shown in Table 7. The small areas of porphyrins **9**, **10** and **11** imply an orientation with the plane of the porphyrin perpendicular to the plane of the air water interface. Table 7 also lists the relative rate of Cu(II) insertion into the various porphyrins in the assemblies, films and in dimethylformamide. The striking observation is that although porphyrin **7** is metalated most rapidly in solution and at the air water interface, the rate is much slower than that of **10** in assemblies. Further, no metalation of **11** is observed in the films and assemblies. Thus it appears that assemblies of **10** exist with the porphyrin plane at hydrophilic–hydrophylic interfaces accessible to Cu(II). Porphyrins **7** and **9** can be metalated readily in films yet undergo a conformational change upon being incorporated into assemblies and become resistant to metalation. The mode of Cu(II) penetration into the assemblies was demonstrated to be a combination of direct penetration of the ions through the film and insertion through imperfections at the edge of the solid support by examining the relative metalation rates at several positions on large glass slides containing assemblies of the porphyrins.

In summary, the various organizates discussed here are capable of dramatically influencing metal

Table 7. Areas of porphyrins **7–11** and relative Cu^{2+} metallation rates in solutions, films and assemblies of the porphyrins

porphyrin	area, Å^2/molec.[a]	rel. metallation rate		
		solution[b]	films	assemblies
7	100	1164	rapid	slow
8	84	1	0	0
9	58	384	rapid	v. slow
10	53	500	rapid	rapid
11	56	10	0	0

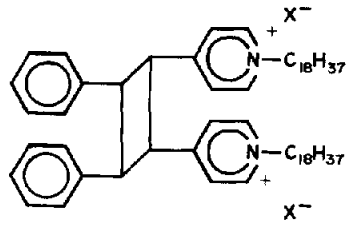
[a] In 1:5 mixture with arachidic acid at 20 dyn/cm. [b] DMF at 50 °C.

chelation reactions. In micelles and microemulsions the presence of cofactors is required to accelerate the metallation of porphyrins. Through careful selection of the mediator, metallation of porphyrins trapped in organizates by a particular metal ion from a solution containing a mixture of metals may be possible. Preferential mediation of this type should be of use in explaining selective biological ion transport processes. In monolayer assemblies, metal ion insertion was shown to depend on the specific orientation of the porphyrin in the assembly; this type of effect has as yet not been demonstrated in other organized media.

Photodimerization in organized media

In addition to isomerization about the double bond, an electronically excited olefin may react with a second ground state olefin to form a cyclobutane dimer. For this bimolecular reaction to occur, the excited olefin must encounter a second ground state olefin sometime within its excited state lifetime. The frequency of encounter is determined by the concentration of olefin, and the rate at which it can diffuse in the medium. Organized media effectively concentrate associated reagents, favoring photodimerization, but could also conceivably restrict their motion, preventing the necessary encounters. Alignment of the olefin in the matrix of some of the more organized systems may also affect the stereochemistry of dimerization by restricting the possible orientations with which the olefins may approach each other.

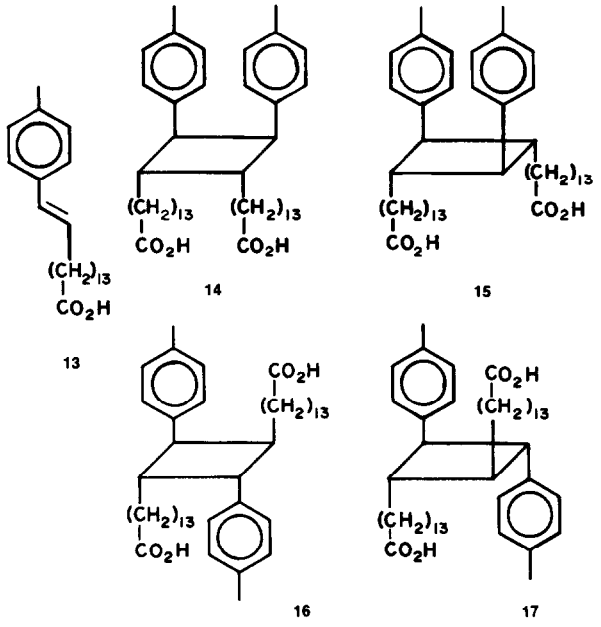
Because of its charged chromophore, the surfactant stilbazole, **2**,[79,80] would not be expected to be a good candidate for photodimerization; intermolecular repulsion should prevent the necessary approach of the olefin moieties for reaction. This appears to be the case in homogeneous and micellar solutions. In acetonitrile and CTAB micelles the only photochemical reactions seen are monomer fluorescence and trans-cis isomerization. Crystals of **2**, X = p-halobenzenesulfonate, and monolayer assemblies, on the other hand show both red shifted (excimer) fluorescence and dimerization, indicating that the electrical repulsion is overcome in these highly ordered systems. Both the rate and the maximum extent of dimerization of **2** in supported monolayer assembly can be reduced by diluting the layers with arachidic acid or tripalmitin, which suggests that lateral motion of the surfactants in the assembly does not occur on the time scale of the irradiation (the order of 1 min). The dimerizations which do occur must result from stilbazoles which are already in contact with each other. A similar reduction in dimerization results from placing "spacer layers" of inactive surfactants between layers containing **2**, indicating that, in unspaced assemblies, intralayer dimerization must take place. Irradiation of crystals of **2** (X = p-halobenzenesulfonate) results in the exclusive formation of a single dimer with the probable structure **12**.



12

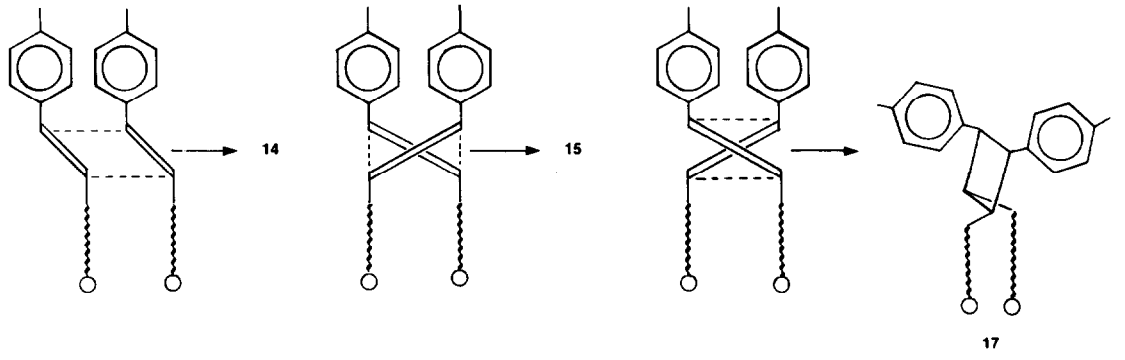
This is unusual in solid state photodimerizations; while solid state photodimerization of stilbazole salts has been investigated, these compounds generally produce head-to-tail products, rather than the head-to-head product shown here.[136,137] It seems likely that this stereochemistry might well result from an unusual heat-to-head orientation of **2** in the crystal which in turn results from a crystal structure affected by hydrophobic interactions of the hydrocarbon chain groups. While the structure of the product of photodimerization in monolayer assembly has not been investigated, It seems likely that incorporation in the assembly would affect its stereochemistry, and in particular that the product of interlayer dimerization might differ from that of the intralayer process.

We have also studied photodimerization of the surfactant styrene, **13**, in various media.[138] As with the stilbene probes, the chromophore of **13** is in a hydrophobic portion of the molecule, and so should be preferentially located in hydrophobic portions of organized media. When spread on the water surface, **13** exhibits behavior very similar to that of unsubstituted fatty acids, compressing at low pressure to a molecular area of about 20 Å^2 at which point the surface pressure increases sharply. This is in accord with an organization of **13** in which the hydrocarbon chains are fully extended and tightly packed into a highly ordered lattice. On a short range the organization of this structure may approach that of



crystalline media. When irradiated in the solid state or monolayer assembly **13** forms a single product (apparently the same product) whose spectra are consistent with cyclobutane structures **14–17**. Solid state dimerization could conceivably yield any of the structures shown, depending on the orientation of the chromophores with respect to each other in the crystal. That only one product is seen is characteristic of solid state photoprocesses and illustrates the uniformity of orientation of molecules in the crystalline array. The fact that only one product is seen in irradiation of monolayer assemblies of **13** suggests a similar regularity of structure and supports the view that monolayers may be a reasonably accurate two dimensional analog of crystals. Irradiation of homogeneous and micellar solutions give a mixture of dimeric products which may contain all four of those shown plus others resulting from cycloaddition of the photoisomerization product cis **13** to trans or cis **13**.

It is helpful to consider the possible structures of the dimeric product in light of what is known about monolayers. Because of the tightness of the fit of **13** into the monolayer it seems most unlikely that the olefinic portions of adjacent layers could approach each other closely enough to result in interlayer dimerization. Such motion would require an increase in the surface area of the layer, which has been shown to be strongly disfavored in monolayers (see sections on photoisomerization, ketones). This effectively rules out **16** as a structure for the product. Either **15** or **17** could conceivably form from intralayer dimerization (see scheme below), however both are unlikely, since they would increase the surface area of the monolayer. In the case of **15**, the carbon carbon double bonds, which start out at a steep angle relative to the monolayer surface become essentially parallel to the surface, at the same time forcing the aromatic groups and the fatty acid chains to a greater distance from each other. In **17** the former carbon carbon double bonds are now at an even steeper angle, however the aromatic groups and the fatty acid chains are again forced to a greater distance from each other. Formation of the remaining



possibility, **14**, should be accompanied by none of the area increases characterizing the other dimers. Although the change in bond angles here is slightly unfavorable, the decrease in distance between the olefin groups becoming cyclobutane should compensate for this, and in fact the product appears here, and should appear to the monolayer assembly very little different from two molecules of **13**. Thus while a firm identification of **14** as the product has not yet been made, we believe it most likely to be the correct structure.

Interfacial electron transfer reactions

Understanding of the photosynthetic process requires a thorough knowledge of the excited state electron transfer and subsequent charge separation processes that initiate photosynthesis.[139–142] Efforts to duplicate the *in vivo* system with artificial membranes such as micelles, vesicles, etc. have derived from (a) a desire to understand the intimate mechanism of photosynthetic electron transport system and (b) recognition that efficient photoinduced charge separation can provide a means of converting solar irradiation into other energy forms (i.e. electrical or chemical). Equations (1)–(4) outline the steps involved in an excited state electron transfer reaction between an excited donor, D*, and an acceptor, A.[143] Excitation of the donor is followed by association of

$$D \xrightarrow{h\nu} D^*; \quad D^* + A \overset{K_a}{\rightleftarrows} (D^* \ldots A) \tag{1}$$

$$(D^* \ldots A) \xrightarrow{k_{et}} (D^+ \ldots A^-) \tag{2}$$

$$(D^+ \ldots A^-) \overset{K_s}{\rightleftarrows} D^+ + A^- \tag{3}$$

$$(D^+ \ldots A^-) \xrightarrow{K_b} (D \ldots A). \tag{4}$$

D* and A to form an "encounter complex". Electron transfer occurs within the complex followed by either back electron transfer of the ions formed or separation of the ions. Surfactant organizates are capable of influencing the association and dissociation equilibria K_A and K_S respectively, via a combination of electrostatic and hydrophobic interactions. As a result examination of effects of surfactants on photoinduced charge separation processes have been broken down into studies of (a) excited state quenching and (b) the thermal back electron transfer reaction.

Excited state quenching processes. In order to discuss reactions between an excited donor and some acceptor in surfactant solutions the distribution of both D and A between the aqueous and aggregate phases must be considered. Many systems that have been examined involve an aromatic hydrocarbon donor (such as pyrene) which has been assumed to reside almost exclusively within the hydrophobic portion if the organizate. The acceptor molecule distributes itself between the aggregate and aqueous phases as shown in Scheme 3. In micelles, the distribution of solubilizates has been shown to follow Poisson statistics.[144, 145] Quenching of the donor excited state by the aqueous acceptor occurs by the typical diffusional processes (eqns 1–4); however, when the micelle contains both the donor and acceptor prior to excitation of the donor, quenching may occur in a purely static fashion or by both static and intramiceller dynamic pathways. The kinetics of the above quenching reactions have been examined by several groups and a review of these kinetic analyses has appeared.[146] At this point is is worthwhile to examine a few examples of varying acceptor distributions that have been documented.

Four general situations result when fluorescent donors are employed (i.e. the excited state decay of the donor is rapid relative to escape of the acceptor from the micelle). The first two cases are ones in which the acceptor, A, is associated strongly with the micelle such that the concentration of the quencher in the aqueous phase may be assumed to be zero. The steady state quenching treatment for the first case, allowing for a statistical distribution of quenchers, has been derived by several researchers[148–152] and is presented below based on the work of Infelta

$$I/I^\circ = (1/k_q\tau_0)_{exp}(-\bar{n}_A)\sum_{i=0}^{i=0}[n_A{}^i/[(1/k_q\,\tau_0) + i]i!] \tag{5}$$

(eqn 5)[152] where τ_0 is the radiative lifetime of D*, k_q is the quenching rate constant, n is the average number of acceptors per micelle and i is the number of acceptors in a micelle. Equation (5) describes the first case, consisting of quenching of the excited state of D by both purely static and an intramicellar dynamic process. Thus steady state quenching of D* in this case exhibits non-linear Stern-Volmer plots (I^0/I vs $[A]_{tot}$). Also the transient donor emission decay appears as a multiple exponential with decay at long times equivalent to decay in the absence of quencher. Rodgers and Wheeler observed such behavior in the quenching of pyrene by copper (II) chloride, methyl viologen, and cetylpyridinium chloride in SDS micelles.[148] Pyrene quenching by a surfactant nitroxyl radical cation strongly associated with both SDS and CTAC micelles was investigated by Singer and Atik.[147] They expressed quenching constants obtained as second order constants and, using the Stokes–Einstein equation, determined microviscosities of the micelle interior.

In the second case the intramicellar quenching predominates; in such instances the degree of quenching increases exponentially with an increase in the average number of quenchers per micelle. The excited state decay in this situation is that of the unquenched excited donor regardless of quencher concentration. Mataga *et al.* observed this behavior for quenching of pyrene fluorescence by N, N-dimethylaniline in the presence of SDS micelles.[154] Turro made use of the simplified quenching kinetics to determine aggregation number of SDS micelles at various ionic strengths by examining the quenching of ruthenium(II) tris(2, 2′-bipyridyl) by 9-methylanthracene.[155].

Theoretical examinations of the role of dimensionality for reactions between two molecules within a micelle have also been presented.[156] The cases considered are (a) diffusion of one reactant to a reactive surface, (b) collision of two reactants both confined within the micelle and (c) the reaction of two reactants restricted to diffusion along the micelle surface. The results indicate that geometric concerns are of major importance in analyzing reactions of this type. The authors compared experimental results for various systems with theoretical results obtained for a micelle having a 20 Å radius and a diffusional rate of $5.0 \times 10^{-7}\,cm^{-2}/s$ and observed good correlation between the type of intramicellar diffusion predicted for their experimental examples and the values calculated given the above parameters.

In the third and fourth cases the micelle solubilized donor molecule is quenched by both micelle bound and water solubilized acceptor species.[146, 150, 151] Infelta has provided a kinetic treatment for such a system maintaining the same assumptions used in the analysis for the case where the quencher is totally micellized.[152] In the third case, once again quenching exhibits non-linear Stern–Volmer behavior as ground state association occurs. However, the excited state decay is somewhat different from the previous case. Here the luminescence will be multiexponential as before but the emission at long times will decay with a slope reflecting partial quenching by the aqueous acceptor. In the fourth case, static quenching dominates the intramicellar process and the emission decay is a single exponential reflecting only quenching by aqueous acceptor. Analysis of the decay of pyrene in SDS micelles in the presence of diiodomethane allows determination of the distribution constant of diiodomethane between micellar and aqueous phases as well as entry and exit rates.[157] Another example of intermicellar quenching of this type, case 4, was recently explored involving quenching of zinc(II) tetraphenylporphyrin by duroquinone in CTAC micelles.[158] The association equilibrium of tertiary amines with non-ionic micelles was examined by Costa *et al.* by probing the amine quenching of aromatic esters solubilized within the micelle.[153]

In addition to studies of rapidly decaying donor species, many systems having chromophores with excited state lifetimes long enough to make determination of the quencher solubilization site during the lifetime of the chromophore impossible have been examined. In other words the quencher is capable of exchanging from one micelle to another during the lifetime of the experiment. An example of such a case is provided by the quenching of ruthenium(II) tris(2, 2′-bipyridyl) by methyl viologen in SDS micelles.[109, 110, 159, 160] In this system, the quenching follows Stern–Volmer kinetics yet the quenching rate is much higher than that in the absence of SDS. Further, the excited state decay of the chromophore is clearly a single exponential implying that all the ruthenium sites "see" the same number of quenchers. One means of explaining this type of excited state decay behavior is to postulate rapid exchange of the quenchers during the lifetime of the excited ruthenium complex. An apparent contradiction between the ruthenium bipyridyl–methyl viologen system and the pyrene–methyl viologen system (where intramicellar quenching occurs) exists as the lifetime of the ruthenium complex is only slightly longer than pyrene. However, the factor controlling the actual amount of quenching observed in the two cases is the fraction of collisions of D* and A that lead to quenching.[181] For the ruthenium–methyl viologen system this fraction must be much smaller than for the pyrene–methyl viologen system and escape of the viologen from the micelle is much more likely. We employed this rapid exchange model in invoking a

simple exchange equilibrium to describe quenching of a surfactant ruthenium bipyridyl complex by methyl viologen in SDS micelles. The exchange equilibrium below expresses the process as exchange with counterions in

$$2S^{+}_{mic} + MV^{2+}_{aq} \rightleftharpoons 2S^{+}_{aq} + MV^{2+}_{mic}$$

solution. It was shown that the exchange equilibrium constant for viologen association with the micelle varies with the specific counterion (*vide supra*).[109, 110] Recently we have examined the quenching of the surfactant ruthenium complex with the more hydrophobic benzylviologen which is expected to bind strongly with SDS. In this case non-linear Stern-Volmer quenching was observed as well as multiple exponential decay of the excited ruthenium complex. The quenching fits the very complex case described by Infelta (*vide supra*) involving both aqueous and micelle bound quenching processes.

In summary, there are a number of factors that influence excited state quenching processes in micellar media. The equilibria of association of both the chromophore and quencher are of primary importance, yet the rate of exchange of the species in and out of the micelle also strongly influences quenching processes. Thus, a quencher may associate strongly with the micelle yet may also escape the micelle very rapidly and thus experience intermicellar rather than intramicellar quenching. Other factors such as quencher hydrophobicity and chromophore decay rate also strongly influence the quenching process in micelles.

Recently examination of light induced electron transfer in media other than micelles has received attention; however, most studies in other media involve charge separation processes and will be discussed subsequently. A number of studies have been done using synthetic vesicles as a microinterfacial medium.[47, 161, 162] The ruthenium bipyridyl–methyl viologen system was examined by Tunelli and Fendler[47] in the presence of dihexadecyl phosphate vesicles. They examined the four possible situations for local of the chromophore and quencher: (a) the viologen is trapped within the vesicle water pool and the ruthenium complex is bound to the outer surface; (b) the opposite of (a); (c) both species associated with the outer surface of the vesicle; (d) both species associated with the inner surface (water pool). They observed quenching to be most rapid when both species were trapped within the inner water pool of the vesicle. The lowest quenching rates were observed for cases (a) and (b) above. In (a) and (b) quenching is believed to occur via a mechanism other than electron tunneling through the phospholipid bilayer of the vesicle.

Charge separation processes. The previous discussion outlines the steps involved preceding the charge separation. Once the excited state electron transfer has occurred the same factors that influenced the initial photoinduced electron transfer now control the thermal back electron transfer (see Scheme 1). Recombination may occur within the aggregates imediately following the photoproduction of the ions or the ions may separate (K_S in Scheme 1) and be subject to the electrostatic and hydrophobic-hydrophilic interactions imparted by the presence of the surfactant. This separation/recombination is a crucial portion of photosynthetic charge transport and is vital to any possible application of synthetic interfaces to photochemical energy storage devices.[142]

Charge separation processes in micellar media have been examined for a large number of systems. Recombination rates for photoproduced ions in a variety of systems are listed in Table 8. As can be seen, the process may follow either first or second order decay kinetics (or complex mixtures of decays). In situations for which the driving force for expulsion of one of the photoproduced species from the aggregate is very small, the recombination of ions is primarily a first order (intramicellar) process. The quenching of ZnTPP by C_{12} MV^{2+} (#2 of Table 8) results in the formation of the very hydrophobic species C_{12} MV^{+} which is readily solubilized within the CTAC micelle and the recombination occurs by a fast first order process.[167] Matsuo has examined the quantum yield for formation of reduced viologen for the system consisting of Ru(C_{12} bpy)2+, a viologen, EDTA (to reduce the Ru^{3+} formed upon quenching by the vologen) and CTAC.[173] They observed that the quantum yield for viologen reduction was 21 times higher for dodecylviologen than for methyl viologen. The quenching is much faster with dodecylviologen and, even though charge separation should be less efficient for the dodecyl derivative, the viologen photoreduction is dominated by the much faster quenching.

Quenching of a micelle trapped chromophore by ions capable of ion pairing with the micelle surface results in either first or second order decay of the reduced ions formed (#1, Table 8). For example, Cu(II) quenching of MPTH in SDS results in strictly second order decay of the MPTH formed; the Cu^{+} formed is rapidly displaced by Cu(II) in the aqueous phase and the intramicellar recombination is

Table 8. Electron transfer quenching and back transfer rates for various substrate-quencher combinations in surfactant solutions

#	sur-factant	chromo-phore[a]	quencher[b]	back reaction	k_b	ref
1	SDS	MPTH	Cu^{2+}	$MPTH^{\cdot+} + Cu^{+}$	$9.3 \times 10^{9} M^{-1}s^{-1}$	165
2	CTAC	ZnTPP	$C_{12}MV^{2+}$	$ZnTPP^{\cdot+} + C_{12}MV^{\cdot+}$	$4.0 \times 10^{6} s^{-1}$	167
3	CTAC	$Ru(C_{12}bpy)^{2+}$	DMA	$Ru(C_{12}bpy)^{1+} + DMA$	$2.6 \times 10^{7} M^{-1}s^{-1}$	168
4	CTAB	pyrene	DMA	$Pyr^{\cdot-} + DMA^{+}$	$\sim 4.0 \times 10^{7} M^{-1}s^{-1}$	169[c]
5	CTAC	$Ru(bpy)^{2+}$	$C_{12}MV^{2+}$	$Ru(bpy)_3^{3+} + C_{12}MV^{\cdot+}$	$8 \times 10^{6} M^{-1}s^{-1}$	170,171
6	SDS	$Pd(TPPS)^{4-}$	MV^{2+}	$Pd(TPPS)^{3-} + MV^{\cdot+}$	$2 \times 10^{9} M^{-1}s^{-1}$	172
7	SDS	$Pd(TPPS)^{4-}$	BV^{2+}	$Pd(TPPS)^{3-} + BV^{\cdot+}$	$5.2 \times 10^{8} M^{-1}s^{-1}$	172

[a] Chromophores are: MPTH = N-methylphenothiazine ; ZnTPP = Zinc tetraphenylporphyrin; $Ru(C_{12}bpy)^{2+}$ = [N,N'-di(dodecyl)-2,2'-bipyridine-4,4'-dicarboxamide)-bis(2,2'-bipyridine]ruthenium (II); $Pd(TPPS)^{4-}$ = palladium(II)-tetra(p-sulfonatophenyl)porphyrin. [b] Quenchers are: $C_{12}MV^{2+}$ = N-dodecylmethyl-4,4'-bipyridine; DMA = dimethylaniline; MV^{2+} = N,N'-dimethyl-2,2'bipyridine; BV^{2+} = N,N'-dibenzyl-2,2'-bipyridine. [c] Estimated assuming an efficiency of charge separation of 1 with all excited pyrenes being quenched and $t_{1/2}$ = 500 μs.

averted.[165] The second order recombination is still quite rapid, however, as the negatively charged micelle carrying the $MPTH^+$ attracts the Cu^+. When Eu(III) is the quenching ion a mixture of intra and inter-micellar recombination processes results.[166]

When one of the products of an intramicellar quenching event is very hydrophilic and bears the same charge as the micelle that species will be expelled from the micelle and recombination can be quite slow (#3 and 4, Table 8). In the examples listed in Table 8 the dimethylaniline cation radical is formed in CTAC micelles and is readily ejected from the micelle. Recombination in these cases[168,169] is observed to be much slower than in homogeneous solution (> 50 fold).

Another approach to generating long lived transients relies on a dramatic change in the hydrophobicity of a water solubilized species subsequent to excited state electron transfer (#5, Table 8). The quenching of $Ru(bpy)^{2+*}$ by the amphiphilic viologen, $C_{12}MV^{2+}$, occurs primarily in the aqueous phase; the reduced viologen, $C_{12}MV^{+}$, is much more hydrophobic and is readily solubilized into the CTAC micelles present. The recombination of the $Ru(bpy)^{3+}$ and the $C_{12}MV^{+}$ is slowed dramatically as a result of electrostatic repulsion.

Addition of a micelle forming surfactant to solutions containing a chromophore and quencher of opposite charge may result in ion pairing of one of the species to the micelle (Table 8, #6 and 7). In such cases the photoproduced ions formed may exhibit similar ion-pairing characteristics allowing long lived transients to be formed. For example, quenching of a tetraanionic palladium(II) porphyrin by either methyl- or benzylviologen in the presence of either SDS or CTAC micelles results in long lived radical ions (no charge separation is observed in the absence of surfactant). The cationic viologen associates with the SDS micelle; here, hydrophobic stabilization of the reduced viologen in the micelle is also important as BV^+ decays more slowly than MV^+.[172]

Examples of charge separation in surfactant vesicles typically involve systems similar to those employed in micelles.[47,161,162,174-176] The primary difference between decay processes in micelle and vesicle systems involves the water pool at the vesicle interior. A vesicle entrapped species that is ejected from the hydrophobic interior upon light induced electron transfer can become trapped within the vesicle's interior aqueous compartment. Kinetics of radical ion processes in vesicles have been examined by several groups.[47,161,177] Escape of $MPTH^+$, subsequent to reductive quenching of a ruthenium bipyridyl complex, into both vesicle entrapped and bulk aqueous phases was examined by Infelta *et al.*[177] Recombination of the $MPTH^+$ in the vesicle entrapped water pools with the reduced

ruthenium complex in the hydrophobic portion of the vesicle was observed to be much faster than decay of MPTH expelled into the bulk aqueous phase (t 1/2 > 1 ms).

Several examples of photoinduced charge separation processes in microemulsions have been described in the recent literature.[163, 164, 178–180]

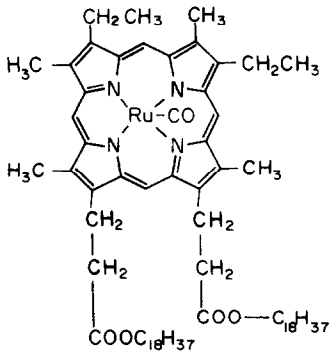
One particularly interesting study involves an examination of the pyrene–dimethylaniline (DMA) system in CTAC micelles, didodecyldimethylammonium bromide (DDAB) vesicles, and oil in water microemulsions in which CTAC was the surfactant employed.[163] The authors relate their observations to the fact that the yield for formation of pyrene anions and dimethylaniline cations increases with increasing dielectric constant of the medium and decreases with increasing viscosity. The yield of photoproduced ions decreases upon increasing the medium viscosity by (a) increasing the CTAC concentration to form rod shaped micelles and (b) using DDAB vesicles. In microemulsions, little charge separation is observed with pyrene–DMA as the relative polarity of the medium is considerably less than that of the cationic micelles. Use of pyrene tetrasulfonate as sensitizer results in an increase in the yield of ions as the more hydrophilic pyrene derivative is solubilized primarily in the polar microemulsion–water interface.

The variety of experimental situations possible in examining excited state electron transfer reactions in organized media is very broad and involves considerations of hydrophobic and electrostatic interactions between two reactants and each reactant and the surfactant aggregate. Much has been learned of the relative influence of the various factors influencing excited state electron transfer processes; the behavior of particular systems (combinations of donors, acceptors and surfactants) can be predicted in many instances. However, very few systems exist that exhibit rapid quenching kinetics, efficient charge separation and greatly hindered recombination reactions.

Ligand exchange reactions of iron and ruthenium complexes

One of the properties of assemblies of monolayers that distinguishes them from the other organizates discussed here is that the assembly exists as a solid support and, as a result, migration of molecules incorporated into the structure occurs slowly if at all.[60] As a result, the supported monolayers provide an excellent medium for trapping and observing reactive intermediates. A particular process in which this feature of the assemblies has been applied is the association of oxygen with porphyrins of the iron family. Most porphyrins from μ-oxo bridged dimers when solutions of the iron (II) species are exposed to oxygen.[182, 183] Recently Collman *et al.* have synthesized an oxygen binding porphyrin that does not undergo this undesireable side reaction.[184]

The mechanism of association of oxygen in solution is believed to involve a pentacoordinate intermediate. In an effort to probe this process we examined the behavior of the complex PRuCO (below) incorporated into monolayer assemblies of cadmium arachidate.[186] The visible absorption



PRuCO

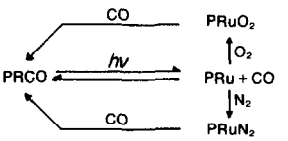
spectrum of PRuCO in the assemblies is identical to that in solution indicating the absence of interporphyrin interactions. Upon photolysis of these assemblies *in vacuo* the spectrum changes revealing the presence of a species very similar to the transient produced upon flash photolysis of the same porphyrin in benzene solution.[187] However, unlike the solution transient the intermediate formed in the assemblies is stable in the absence of ligands and represents the decarbonylated complex PRu.

Exposure of the complex to carbon monoxide regenerates PRuCO. If, instead, nitrogen is introduced, the heretofore unobserved complex $PRuN_2$ is formed. The dinitrogen ligand is slowly displaced by CO in the absence of light and rapidly exchanges upon photolysis with visible light. The intermediate PRu also reacts with oxygen to form the dioxygen complex, also displaced slowly by CO in the dark and quickly with light. The processes are sumarized in Scheme 4 below.

We have also examined thermal ligand exchange processes of iron(II) and iron(III) porphyrins in assemblies. Both the iron(II) porphyrins we examined (below) are unstable in solution at room temperature (forming the μ-oxo dimer). The iron(III) species are stable in solution and at air–water interfaces and can be readily incorporated into assemblies. The nature of the alkyl group is important in hindering μ-oxo dimer formation of the iron(III) species at the air–water interface. This is illustrated through the observation that the iron(III) meso-tetra(4-carboxyphenyl)porphyrin tetraoctadecyl ester readily undergoes μ-oxo dimer formation[188] whereas the bulky dihydrocholesterol ester (above) does not dimerize at the air–water interface.

Assemblies of Fe(III) TCP–TDE and Fe(III) PF–THA both exhibit absorption spectra in only slightly red shifted relative to solution ($CHCl_3$). Exposure of either to piperidine vapor *in vacuo* results in immediate formation of iron(II) bispiperidinate (Fig. 11). Exposure of the reduced assemblies to CO results in a small red shift in the beta absorption band of the porphyrins as expected for substitution of piperidine by CO. However, addition of dioxygen to the bispiperidinate results in no immediate spectral change; oxidation of the porphyrin to the monomeric iron(III) species occurs slowly with some decomposition.

An alternative approach to reduction of the iron(III) porphrins in solution involves treatment with nitric oxide in methanol. The iron(II) nitrosyl porphyrins are formed in this process.[189, 190] Reduction of assemblies of Fe(III) PF–THA by sequential exposure to NO and methanol was attempted. An immediate red shift in the porphyrin beta absorption band occurred upon exposure to nitric oxide giving Fe(II) PF–THA NO^+ (Fig. 12). Evacuation of the Fe(II)–NO^+ species resulted in the reappearance of the iron(III) complex. Addition of methanol vapors to the nitrosyl complex gives the starting iron(III) porphyrin. Thus neither piperidine reduction or nitric oxide/methanol reduction leads to a species



Scheme 4.

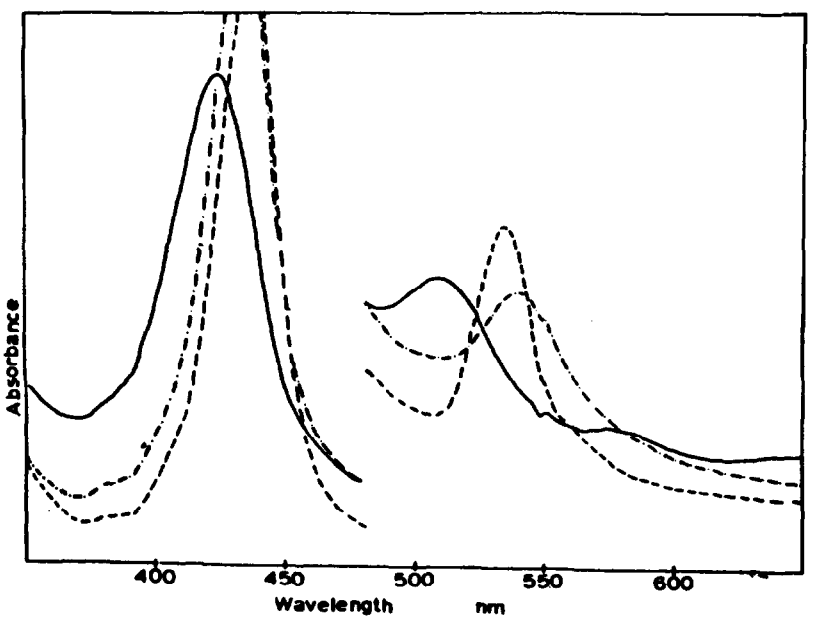
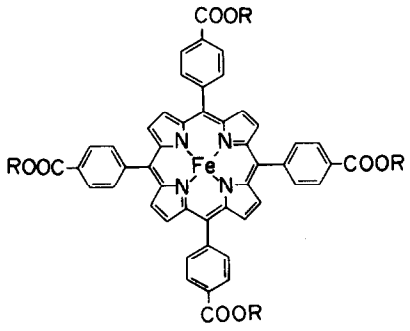
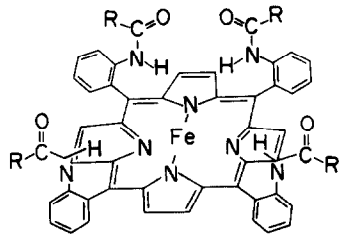


Fig. 11. Absorption spectra of Fe(III)PF-THA before (–) and after addition of piperidine vapors followed by addition of CO(– · –).



R = dihydrocholesterol
Fe(III)TCP-TDE



R = hexadecyl
Fe(III)PF-THA

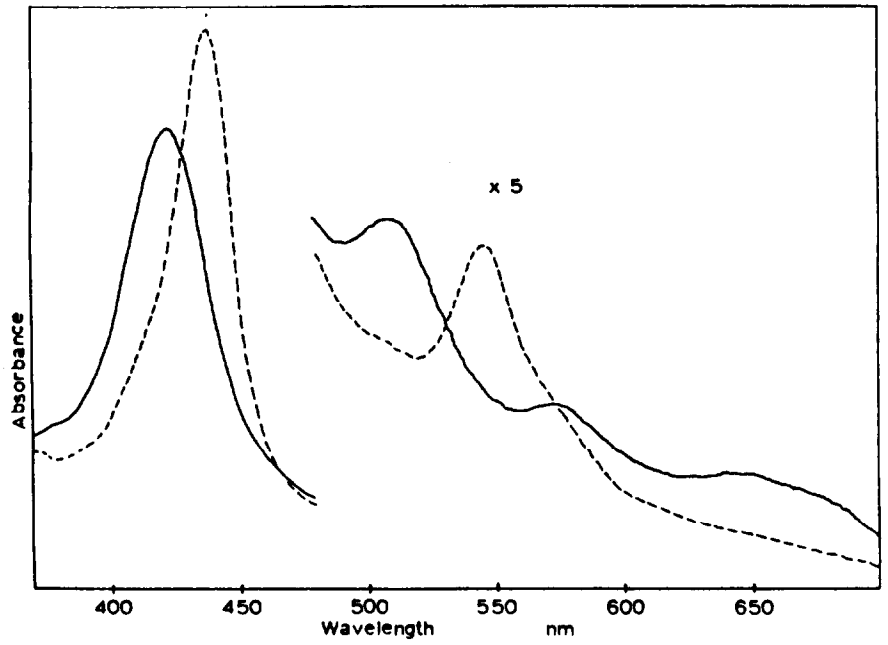


Fig. 12. Absorption spectra of assemblies of Fe(II)PF-THA before (—) and after (---) exposure to nitric oxide.

capable of reversibly binding oxygen in monolayer assemblies. In solution bispiperidyl complexes of iron(II) porphyrins do yield dioxygen adducts at two temperatures[192] indicating a fundamental difference between solution and assembly reactivity.

The ability of monolayer assemblies to provide a rigid matrix for isolating reactive intermediates has been demonstrated in this section. Further, the generation of complexes not observable in solution also appears in the built up films. The use of assemblies as rigid matrices is also elegantly demonstrated in the work of Kuhn.[60,191]

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