CHARGE SEPARATION IN PHOTOREDOX REACTIONS

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ABSTRACT

The structural aspects controlling charge separation in molecular photoionization reactions in organized molecular assemblies involving micelles, reverse micelles and vesicles are being studied by optical and electron magnetic resonance techniques including the time domain technique of deuterium electron spin echo modulation (ESEM) and matrix proton electron nuclear double resonance (ENDOR) to measure weak electron-nuclear dipolar interactions. ESEM and matrix ENDOR are particularly well adapted to the study of disordered systems as exemplified by micelles and vesicles. In addition to conventional studies by optical absorption and electron spin resonance, ESEM and matrix ENDOR complement each other and enable independent detection and analysis of extremely weak electron-nuclear dipolar interactions which give structural information often not available by other experimental techniques. The complementarity of using both these techniques greatly strengthens the conclusions reached. Since dipolar interactions are averaged out by molecular tumbling in liquid solutions, their exploitation requires studies in rapidly frozen solutions. A variety of experiments has shown that micellar and vesicular structure is retained in these rapidly frozen solutions. Most recently the conformation of x-doxylstearic acid spin probes has been studied as a function of x in cationic and anionic vesicles in liquid solution by a complex simulation of the electron spin resonance lineshapes. The conformation changes with x and with vesicle charge type are the same as independently measured in frozen solutions by variations of the deuterium electron spin echo modulation depth. This shows that embedded photoionizable molecules in frozen vesicle solutions that have similar locations and conformations as in liquid vesicle solutions.

The photoionization yields of alkylphenothiazines in micelles and vesicles have been shown to depend on the alkyl chain length and to correlate with relative distances from the surfactant assembly interface measured by deuterium ESEM and matrix proton ENDOR. The trends are opposite, but understood, in micelles versus vesicles because of the higher disorder of the surfactant alkyl chains within micelles. Thus the location and photoyields can be controlled by the alkyl chain length. This has been confirmed by similar measurements on the photoionization of alkyltrimethylbenzidines in surfactant assemblies. Fine tuning of this location control can be achieved by addition of suitable cosurfactants such as cholesterol.

The photoionization of alkylmethylviologens versus alkyl chain length has also been studied in vesicles, micelles and reverse micelles. The results and interpretations are consistent with the photoionization studies. Other photoionization studies include alkylpyridiniumtriphenylporphyrins in vesicles, tetramethylbenzidine in mixed ionic/nonionic micelles, tetramethylbenzidine in anionic micelles in the presence of crown ethers that complex the counterions, and (phenothiazinylalkyl)- and (carbazoylalkyl)trimethylammonium bromides in aerosol dioctyl (AOT) reverse micelles.

Nitroxide spin probes have been used to study the degree of water penetration into mixed ionic/nonionic poly(ethylene oxide) and cationic/anionic micelles by using ESEM methods and selectively deuterated surfactants. The effect of urea interaction at micellar interfaces on the interface hydration has also been evaluated by studying nitroxide probes with ESEM. The amount of water and isooctane solvent penetration into AOT reverse micelle interfaces has also been assessed by ESEM by using deuterated water and deuterated isooctane. Finally, the effect of cholesterol on the anionic and

cationic vesicle interface structure has also been studied by spin probe methods. These spin probe studies lead to predictions about the photoionization efficiency in such systems.

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CHARGE SEPARATION IN PHOTOREDOX REACTIONS

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1. Introduction

All available energy resources need to be optimized for the economic production of energy in useful forms for mankind. Thus far, light energy has been only minimally utilized. The effective utilization of light energy probably depends largely on appropriate conversion and storage methods. Some current goals involve photoredox reactions to generate a fuel from a cheap abundant nonfuel and direct conversion to electricity. Nature's light storage example is the photosynthetic process in the first step of which chlorophyll is photoionized to result in net charge separation. In an artificial system a key requirement is to achieve net charge separation, since efficient photoionization followed by rapid ion recombination is not a route to practical energy storage. In homogeneous solution rapid ion recombination back reactions are difficult to counteract. In photosynthesis the back reaction is largely prevented by sequential electron transfer to several electron acceptors within an organized molecular assembly. However, even though the x-ray diffraction structures of several bacterial photosynthetic reaction centers have been determined, the essential structural features controlling the electron transfer are not fully understood. Perhaps this is due to the complexity of these systems. In our current work we are attempting to obtain a better molecular understanding of the structural aspects controlling charge separation in photoredox reactions in simpler organized molecular assemblies such as micelles, vesicles and reverse micelles.

Early objectives focused on modifying the surfactant assembly interface to enhance the photoionization efficiency of embedded molecules. Principal

aspects involved modification of the charge of the interface, the charge density, the surfactant structure, the addition of surface-active additives which changed the local water concentration at the interface and the addition of surface-active molecules which complex counterions to change the local ionic strength near the interface. In the past three years we have focused primarily on developing location control of the photoionizable molecules within the surfactant assemblies with respect to the interface and thereby control the photoionization efficiency. This is done by developing synthetic methods to add variable length alkyl chains to suitable photoionizable molecules. Coincident with this, we have utilized electrostatic interactions between the surfactant assembly and the photoactive molecule to affect the relative locations of the photoactive molecule. We have also developed fine tuning of this location control by modifying the penetrability of the surfactant assembly interface with added cosurfactants that modify the interface structure.

In order to monitor that location control is actually achieved in such experiments our approach has been to measure the weak electron-nuclear dipolar interactions between the paramagnetic photoactive molecule ion and magnetic nuclei in the interfacial region. We have shown that this can be done by using a pulsed electron spin resonance (ESR) technique called electron spin echo modulation (ESEM) in which interactions between the unpaired electron on the photoionized paramagnetic molecular ion are measured relative to deuterium nuclei in water at the interface or in other locations. We have previously shown how this electron spin echo modulation approach can be successfully used to deduce the surrounding structure of paramagnetic species in frozen solutions and how it can be used to monitor the location of a photoproduct ion in surfactant assemblies such as micelles and vesicles. Even though this is relatively well documented, it is even

more convincing to use another independent technique to measure the weak electron-nuclear dipolar interactions which further validates the electron spin echo method.

During the last three years we have had success in doing this by developing matrix proton electron nuclear double resonance (ENDOR) to measure electron-proton dipolar interactions. Changes in these interactions correlate with relative distance changes. The general idea is shown in Figure 1 where a micelle or vesicle consisting of protiated surfactant molecules is formed in a D_2O solution. If the photoionizable molecule moves into the surfactant assembly with increasing alkyl chain length as is illustrated in Figure 1, the electron-deuterium interactions decrease which can be measured by deuterium electron spin echo modulation, while the electron-proton interactions increase which can be measured by matrix proton ENDOR. We have been able to demonstrate in several systems that there is a correlation between the deuterium ESEM results and the matrix proton ENDOR results. Also we have found systems, which will be described below, where the effect of the alkyl chain is the opposite so that a longer alkyl chain 'pushes' the photoionizable molecule more out of the surfactant assembly. This different distance change is also verified by complimentary ESEM and ENDOR measurements.

During this report period we have focused on the synthesis and photoionization of a series of alkylphenothiazines and alkyltrimethylbenzidines which demonstrate that location control via variable length alkyl chains can be achieved and monitored. Photoreduction of alkylmethylviologens has also been studied as well as the photoionization of other selected molecules in micelle, vesicle and reverse micelle surfactant assemblies. We have also continued to use stearic acid nitroxide spin probes to study certain aspects of

Vesicle

Figure 1. Schematic of alkyl chain length effect on photoionizable molecules in vesicles showing direction of location change with increasing alkyl chain length.

the structure of these surfactant assemblies and how these structural features are related to the photoionization efficiency of solubilized molecules.

During the past three years of this project 30 papers have been published and 34 conference and seminar presentations have been given in these areas. Citations are given in Sections 7 and 8. Sections 2 to 6 summarize the highlights of these results. this significant progress has been possible in large part to excellent coworkers that have been supported by the DOE grant and that have brought their own support.

The principal investigator has spent an average of 10 % of the academic year and 100 % of one summer month on this project each year.

2. Photoionization of Alkylphenothiazines

The synthesis of three types of alkylphenothiazines has been developed for this research as shown in Figure 2. The neutral alkylphenothiazines have the greatest variability of alkyl chain length in this series. In addition, we have synthesized negatively and positively charged alkylphenothiazines in which the N-alkyl group is terminated with a negatively charged sulfonate group or with a positively charged trimethylammonium group. The charged group of these alkylphenothiazines serves to anchor the alkyl chain to a charged interface of a micelle or vesicle and affect the location of the photoionizable phenothiazine moiety.

In order to measure the electron-nuclear dipolar interactions by ESEM or by ENDOR it is necessary to work in frozen solutions in which the dipolar interactions are not averaged out as they are in liquid solutions. We have shown in extensive studies over several years that the micellar and vesicular structure is retained in rapidly frozen aqueous solutions. We have recently

Figure 2. Synthesis of alkylphenothiazines, phenothiazine alkylsulfonates and phenothiazine alkyltrimethylammonium bromides.

carried out new lineshape simulation studies of x-doxylstearic acids in liquid vesicle solutions where the doxyl group containing a nitroxide moiety is located at different positions along the stearic acid chain and have shown that the position of the doxyl group with respect to the interface in positively and negatively charged vesicles shows the **same** quantitative trend in liquid vesicle solutions as it does in frozen vesicle solutions where this was measured by electron spin echo modulation. In these frozen solutions the total photoyield can be easily measured by the doubly integrated ESR intensity of the photoproduced radical ion. In general we find that the photoyield trends follow the deuterium modulation depth trends measured by deuterium ESEM. This means that the photoyield is enhanced by a stronger interaction with water at the interface of the surfactant assembly.

Studies of the photoionization of N-alkylphenothiazines in anionic alkyl sulfate and in cationic alkyltrimethylammonium bromide micelles show the initially surprising results that the photoyield and the deuterium modulation depth results both increase with alkyl chain length. This is interpreted as the pendent alkyl chain of the phenothiazine acting to "push" the phenothiazine moiety more towards the surfactant interface. This steric effect dominates the hydrophobic effects of the alkyl chains. This is a consequence of the high disorder of the surfactant alkyl chains constituting micelles in which it is difficult for a longer alkyl chain of an embedded molecule to penetrate more into the micelle interior. Hence the longer alkyl chain actually "pushes" the phenothiazine moiety towards the micellar interface. This interpretation is supported by the observation that in vesicle assemblies the trend in location relative to the interface with the alkyl chain length of the N-alkylphenothiazines is just the opposite. In the more

highly ordered interior of the vesicles, the alkyl chain of the alkylphenothiazines can penetrate more easily and "pull" the phenothiazine moiety more deeply into the vesicle as the alkyl chain length increases due to the favorable hydrophobic interactions with the surfactant alkyl chains.

When the alkylphenothiazines have a charged sulfonate or trimethylammonium group on the end of the alkyl chain, the location of the phenothiazine moiety is controlled by alkyl chain bending because the charged group is located at the vesicle interface. This effect is much more clear in vesicles than in micelles. The amount of chain bending also depends on the interface charge of the vesicle. When the interface charge of the vesicle is the same as the charge on the end of the alkyl chain attached to the phenothiazine moiety, there is more chain bending because of electrostatic repulsion between the surfactant molecule charged headgroups and the charged group on the alkylphenothiazine. When the charge on the surfactant and the charge on the end of the alkyl chain attached to the phenothiazine moiety are opposite, the electrostatic attraction causes the alkyl chains to be closer together and there is less chain bending. This interesting observation holds for either positively or negatively charged vesicle interfaces with either positively or negatively charged groups on the alkyl chain attached to the phenothiazine moiety. Thus, location control can be achieved by varying the alkyl chain length, by varying the surfactant assemblies from micelles to vesicles and by varying the charge of both the surfactant assembly and the alkylphenothiazine molecules.

The photoionization of N-alkylphenothiazines was also studied in sodium bis(2-ethyl-1-hexyl) sulfosuccinate (aerosol dioctyl or AOT) reverse micelles where the interior water pool size of the reverse micelle was varied. The photoyield shows a dependence on the length of the alkyl chain and also

shows a decrease as the interior water pool size increases. This is interpreted as showing that hydration of sodium counteranions with increasing interior water pool size results in an increase of the net anionic charge density of the interface which increases the barrier for electron transmission. Electron spin echo modulation studies in D_2O verify this interpretation which is also further verified with matrix proton ENDOR studies. Consequently, optimization of the charge separation of the photoproducts is best achieved by minimizing the size of the interior water pool in reverse micelles.

The effect of cholesterol as a cosurfactant on the photoionization of neutral alkylphenothiazines in variously charged vesicles was also studied. The addition of cholesterol to positive, negative and neutral types of vesicles reduces the photoyield for the alkylphenothiazines. This is supported by electron spin echo modulation results and is consistent with an ordering effect of cholesterol which allows deeper penetration of the alkylphenothiazine into the vesicle in the presence of cholesterol.

The effect of urea as a cosurfactant has also been studied on the N-alkylphenothiazine photoyield in both micellar solutions and vesicle solutions because of its specific surface-active properties. In both micelles and vesicles the highest yield is obtained for about 1 molar urea or alkyl-substituted ureas. Higher concentrations of urea decrease the photoyield. This is interpreted in terms of urea displacing water at the interface of the surfactant assembly.

3. Photoionization of Alkyltrimethylbenzidines

We have extensively studied the one-photon photoionization of N,N,N',N'-tetramethylbenzidine in micellar and vesicular solutions. In this work the benzidine moiety was functionalized at an N-alkyl position forming the class of

neutral asymmetric molecules, N-alkyl,N,N',N'-trimethylbenzidines (C_n TMB). The three step synthesis procedure is shown in Figure 3. C_n TMB molecules with $n = 1 - 16$ have been synthesized.

Photoionization of the C_n TMB molecules has been studied in anionic sodium alkylsulfate micelles and cationic alkyltrimethylammonium chloride micelles prepared in deuterated water. Deuterium electron spin echo modulation shows that the photoionizable benzidine moiety is moved closer to the micelle interface as the alkyl chain length increases. This is exactly the same kind of trend found for photoionization of alkylphenothiazines in micellar systems. For the alkyltrimethylbenzidines this trend is corroborated by independent measurements of the matrix proton ENDOR linewidth versus alkyl chain length. However when one measures the photoyield, it is found that it is approximately constant with alkyl chain length. This is in striking contrast to the definite photoyield change observed in the alkylphenothiazine system.

A model rationalizing these photoyield differences is shown in Figure 4 which shows different solubilization orientations for these two types of molecules near a micelle interface. Because of the different position of the alkyl chain with respect to the oval shape of the photoionizable moiety the orientations shown seem probable. An electron escape cone can be drawn from the center of the benzidine or phenothiazine moiety, through the width of the spin distribution that intersects the micellar interface. It can be seen qualitatively that the electron escape cone angle will change much more slowly with position for the C_n TMB molecules compared to a more rapid change for the alkylphenothiazine molecules. Quantitative estimates based on this simple geometric molecule indicate a tenfold difference. Thus for alkylphenothiazines the photoyield changes significantly with position relative

Synthesis of N-Alkyl, N,N',N' trimethylbenzidine

Figure 3. Synthesis of N-alkyl, N,N',N'-trimethylbenzidines.

Figure 4. Schematic cross section of a spherical micelle with solubilized alkyltrimethylbenzidine (C_nTMB) and N-alkylphenothiazine (PC_n). The electron escape cone is drawn from the center of the benzidine or phenothiazine moiety through the micellar interface intersecting the moiety. The benzidine moiety solubilizes with its long axis along a micellar radical line, while the phenothiazine moiety solubilizes with its long axis perpendicular to a micellar radical line.

to the interface, whereas for alkyltrimethylbenzidines the photoyield changes very little. This is what is found experimentally.

In unpublished work the photoionization of the alkyltrimethylbenzidines in neutral, cationic and anionic vesicle systems follows the same trend as found earlier for the alkylphenothiazines. Namely, the photoionizable moiety is "pulled" more toward the center of the vesicle away from the interface with increasing alkyl chain length.

4. Photoreduction of Alkylmethylviologens

Dimethylviologen and alkylmethylviologens are readily reduced by near ultraviolet light in both vesicular and micellar assemblies. In solution the photoreduction of dimethylviologen dichloride proceeds through a charge transfer process involving the chloride counterion. The source of the electron for the photoreduction is the negative counterion. This seems to also play a role in surfactant assemblies unless the viologen moiety penetrates significantly into the surfactant assembly such that the chloride ion is too far away to provide the electron. A study has been made using ESR to monitor the concentration of photoreduced viologen produced with a wide variety of counterions in frozen aqueous solutions. By precipitating out the chloride counterion with silver ion, it is shown that the viologen can be reduced by electron transfer with other counterions and also with ionic surfactant headgroups. Thus in vesicle solutions it is considered that the surfactant headgroup is a major source of the electron that results in photoreduction of the alkylmethylviologens.

The availability of a variety of alkyl chain lengths in the alkylmethylviologens from approximately C_1 to C_{16} made this series of molecules good candidates for assessment of alkyl chain length effects on the

location of the photoreducible moiety with respect to a surfactant assembly interface. In fact, such alkyl chain length effects were first demonstrated in our laboratory in collaboration with Jim Hurst and his research group.

In cationic micelles the photoreduction yields for alkylmethylviologens initially increase with increasing alkyl chain length up to about C₁₀ and then decrease. This seems to be correlated with changes in location as indicated by both deuterium electron spin echo modulation data and matrix proton ENDOR linewidth data which show that the location of the viologen moiety actually gets further from the micellar interface as the alkyl chain length increases and then beyond C₁₀ the location moves back towards the micellar interface. These results indicate that as the alkyl chain length is extended the viologen moiety solubilizes further into the hydrocarbon region of the micelle away from the interface. Increasing the separation between the viologen acceptor and the chloride ion donor at the interface therefore results in a greater photoreduction yield which implies that back electron transfer dominates the net photoyield in this case. This is a good example of where **independent** information on location changes with alkyl chain length and on photoyield changes with alkyl chain length are necessary to interpret the physical results. In anionic alkylsulfate micelles the photoreduction changes of the alkylmethylviologens with alkyl chain length are similar, but the location changes are not as significant as they are in the cationic micelles. Since the viologen is a dication, this can explain the difference between these two charge types of micelles.

Photoreduction of the alkylmethylviologens in both cationic dioctydecyldimethylammonium chloride vesicles and anionic dihexadecylphosphate vesicles has also been studied. In both cationic and anionic vesicles the viologen photoreduction yield increases with increasing

alkyl chain length. This is correlated with deuterium electron echo spin modulation and matrix proton ENDOR linewidth measurements that indicate that the viologen moiety penetrates more deeply into the vesicle with increasing alkyl chain length. This is the same location change trend observed with photoionizable molecules in vesicle systems. So generally in vesicles the hydrophobic interaction of longer alkyl chains "pulls" the photoreactive moiety more into the interior of the vesicle. This generality indicates that location control by increased alkyl chain lengths is about the same for a variety of photoionizable and photoreducible molecules in vesicle systems, whereas in micelle systems location control is more complex.

The effect of added cholesterol on the net photoreduction yield of alkylmethylviologens was also studied in both cationic and anionic vesicles. In cationic vesicles the effect of cholesterol, which acts as a cosurfactant and intercalates into the interface of the surfactant assembly, is to decrease the net positive charge density at the interface and consequently decrease the photoyield. However the alkyl chain length effect is stronger than the cholesterol effect. Thus cholesterol acts to fine tune the location control exerted by a change in the alkyl chain length. In anionic vesicles the effect of cholesterol is opposite; cholesterol causes some increase in the photoreduction yield. This is due to a decrease in the effective negative charge density of the vesicle as a result of intercalation of the cholesterol molecules into the bilayer. The different effects of cholesterol for photoreduction in cationic versus anionic vesicles gives a consistent picture when considering that electron transfer through the interface occurs. The effects of α -tocopherol, another cosurfactant, on the photoreduction of alkylmethylviologens in cationic vesicles have also been investigated. It

affects the photoyields but also participates directly in the photochemistry which is a complicating factor.

5. Other Photoionization Studies

We have previously studied the photoionization of chlorophyll and zinc tetraphenylporphyrin in vesicle systems. Although photoionization does occur with visible light which is of practical interest, the yield is relatively low in frozen solutions. Thus we have been interested in using alkylporphyrins to affect the location of the porphyrin moiety with respect to the surfactant assembly interface and increase the net photoyield. A limited study was carried out on three alkylpyridiniumporphyrins that were synthesized in our laboratory with C_9 , C_{12} , and C_{16} alkyl chains. The photoyields were still too small to observe electron spin echo modulation but some information was obtained on differential locations using optical absorption spectroscopy and photoyields were measured by ESR.

With bulk water at the vesicle interface as the electron acceptor, there is an overall decrease in the photoyield as the alkyl chain length increases which implies increasing penetration into the vesicle. However the amount of penetration seems to be relatively small. When tetrabromobenzoquinone and potassium ferrocyanide were used as specific molecular electron acceptors and the photoionization yields were found to decrease. This was interpreted in terms of efficient back electron transfer from the electron acceptor to the alkylpyridiniumporphyrin and implied that the alkylpyridiniumporphyrin did not penetrate significantly into the vesicle interface.

It appears that a less polar alkylporphyrin is desirable to obtain better penetration into the vesicles and better control of the photoyields by

variation of the alkyl chain length. This is a target area for further investigation.

The photoionization of (phenothiazinylalkyl)trimethylammonium bromide and (carbazoylalkyl)trimethylammonium bromide in frozen solutions of aerosol dioctyl (AOT) reverse micelles has also been studied. In addition to small alkyl chain length effects, the greatest degree of photoionization control is achieved by variation of the mole ratio of water to AOT. The maximum photoionization is found for a ratio of five due to enhanced water interactions with the solute and to increased water disorganization at the interface. The water interactions were monitored by the deuterium electron spin echo modulation depth. Little alkyl chain length effect was seen for the phenothiazine derivatives which was consistent with earlier studies on phenothiazine alkylsulfonates in these reverse micellar systems. For the alkylcarbazoyls a weak alkyl chain length was observed which seems related to orientation differences of the cabazoles relative to the AOT/water interface.

A study was also made on the effect of various concentrations of crown ethers on the interfacial potential of sodium dodecylsulfate micelles in which tetramethylbenzidine was used as a photoionizable molecule. Matrix proton ENDOR linewidth changes show that as the concentration of the crown ether increased the tetramethylbenzidine moves toward the micelle interface. This location change correlates with a reduction in the interfacial ionic strength caused by complexation of the surfactant counterions by the crown ethers. The matrix ENDOR results also show that the addition of crown ethers does not affect the degree of hydration of the interface significantly. The broader ENDOR linewidth observed in lithium versus sodium dodecylsulfate micelles suggest that there is greater hydration at the interface of lithium versus sodium dodecylsulfate micelles. This is consistent

with previous results based on other techniques.

Photoionization of tetramethylbenzidine has also been studied in mixed micelles of ionic and nonionic surfactants. This study focused on the photoionization of TMB as a function of the composition of mixed micelle. By using a mixed micelle of ionic and nonionic surfactants it was possible to change continuously the micelle surface charge from a positive net charge to a negative net charge without changes in the size of the micelles as in the case for mixed micelles formed by ionic surfactants. It was found that the photoyield was enhanced in the presence of mixed micelles with a net positive charge since electron escape from micelles is facilitated in cationic frozen micelles. However, it was found that the charge effect is produced only in mixed micelles rich in the cationic surfactant. In these mixtures the most important contribution to the photoyield is the charge of the micelle, while local interactions with water at the micellar interface seem to have secondary importance. However for mixed micelles with a net negative charge the most important contribution to the photoyield is the TMB^+ -water interaction as measured by deuterium electron spin echo modulation.

6. Nitroxide Spin Probe Studies of Vesicle/Micelle Structure

The use of x-doxylstearic acid nitroxide spin probes has continued to be important to probe the structure of frozen micellar and vesicular systems and to relate this to structural aspects controlling the photoionization of embedded molecules in the surfactant assemblies. A study was made using these spin probes in frozen reverse micellar solutions of aerosol dioctyl (AOT) in isooctane as a function of water pool size with deuterium located either in the isooctane or in the water. The results determine the probe location and show that the doxylstearic acid headgroup and the C_8 -TMPO nitroxide spin probe

solubilized at the micellar interface close to the AOT polar headgroup. The trend of the deuterium modulation depth as a function of the doxyl position x in a series of x -doxylstearic acid spin probes shows that the stearic acid chain has an extended conformation for various water pool sizes. In other words the stearic acid chain is not U-shaped or bent as has been found in some vesicle systems. Analysis of the deuterium modulation depth as a function of the AOT water pool size gives good agreement with the current structural picture of AOT reverse micelles in liquid solution. This demonstrates at a molecular level that the micellar structure is retained during the fast freezing used to form the reverse micelle. In particular, it was found that the water molecules associated with the AOT polar headgroup increase up to a ratio of water to AOT equal to 15 and stabilized for this ratio greater than 20. Thus, about 20 water molecules are associated on the average for each AOT polar headgroup for a water to AOT ratio greater than 20.

The structure of mixed micelles formed from anionic and cationic and from ionic and nonionic surfactants was also studied with a series of x -doxylstearic acid spin probes. The doxylstearic acid spin probes have a bent conformation in all of the pure and mixed micellar systems studied. In sodium dodecylsulfate and dodecyltrimethylammonium chloride mixed micellar systems the electrostatic interaction among the surfactant headgroups causes the expulsion of water molecules and an increase in the microscopic viscosity of the interface of the mixed micelle. The extent of these effects depends on the mixed micelle composition. In nonionic/ionic mixed micelles with hexakis(ethylene glycol)monododecyl ether it has been found that both sodium dodecylsulfate and dodecyltrimethylammonium chloride solubilized with their polar headgroups in the ethylene oxide region of the nonionic surfactant. From the trend of the normalized deuterium modulation depth as a

function of the doxyl position and from a comparative analysis of the modulation depths in the mixed micelles with the nonionic surfactant selectively deuterated in the alkyl chain or in the ethylene oxide region, it is found that dodecyltrimethylammonium polar headgroups were located close to the core region, of the mixed micelle near the fifth and sixth ethylene oxide of the nonionic surfactant, while sodium dodecylsulfate polar headgroups are located in a more hydrophilic region close to the second to third ethylene oxide of the nonsurfactant.

The effect of urea addition on the structure of anionic and cationic micellar solutions has also been studied with x-doxylstearic acid spin probes. It is found that added urea does not affect the bent conformation of the doxylstearic acid spin probes in both anionic or cationic micelles. However the analysis of deuterium modulation depth shows that the urea interacts with surfactant polar headgroups at the micellar surface. It is found that the interaction with urea is greater with cationic dodecyltrimethylammonium bromide than with anionic sodium dodecylsulfate surfactants. These results support recent molecular dynamics and Monte Carlo calculations and are in agreement with a direct mechanism of action in which the urea displaces some water molecules and solvates the hydrophobic chains and the polar headgroups of the amphiphiles.

Many experiments have been carried out on the photoionization of various molecules in anionic dihexadecylphosphate (DHP) vesicles and cationic dioctadecyldimethylammonium chloride (DODAC) vesicles. By using x-doxylstearic acid spin probes and vesicles prepared in D_2O , it was found that the deuterium modulation depths were greater for DHP than for DODAC vesicles. This indicates that the DHP vesicle structure is less tightly packed with less chain bending. Upon addition of cholesterol to DHP

vesicles the degree of hydration of the spin probes near the interface is increased while the degree of hydration of spin probes located deeper inside the bilayer is decreased. Upon addition of cholesterol to DODAC vesicles the degree of hydration is decreased for all spin probes. This indicates that cholesterol has different effects on the photoionization yields in DHP versus DODAC vesicles as has been found independently.

Finally as mentioned in the introduction, a detailed ESR lineshape analysis of x-doxylstearic acid spin probes in DODAC vesicles has been carried out in liquid solution. The spectra are well reproduced using the microscopic order/macroscopic disorder model of Freed and coworkers with Brownian rotational diffusion. The partial averaging of the magnetic interactions by local anisotropic motions in vesicles is quantified mainly by an order parameter and by the rotational diffusion rate perpendicular to the alkyl chain. The simulation showed that the doxyl position becomes progressively less ordered as x in x-doxylstearic acids increases up to $x = 12$ but becomes more ordered for $x = 16$. This suggests a U-shaped bent conformation of the doxylstearic acid chain. The rotational diffusion rate shows a similar but inverse correlation and supports the changes in the order parameter. This U-shaped conformation of the spin probe alkyl chain in liquid vesicle solutions is the same as deduced previously in frozen vesicle solutions measured by electron spin echo modulation spectroscopy. This directly demonstrates that the location and conformation of doxylstearic acid spin probes is the same in frozen and liquid vesicle solutions which not only implies that the vesicle structure is retained, but also that the location of embedded molecules and their conformations are retained in the frozen solution.

Unpublished results on the x-doxylstearic acid ESR lineshape analysis in liquid anionic dihexyldecylphosphate vesicles also show a correlation between frozen and liquid solution conformations. In this system the x-doxylstearic acid chain is more extended than in the cationic DODAC vesicle solutions, and this difference is observed in both the liquid and frozen vesicle solutions. This further substantiates that the conformation of embedded molecules in the frozen vesicles studied in the photoionization work bears a close relation to the structure and conformation in liquid vesicle solutions.

7. Publications

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30. Chris Stenland and Larry Kevan, Electron Spin Resonance, Electron Spin Echo Modulation and Electron Nuclear Double Resonance Studies of the Photoionization of N-Alkyl, N,N',N'-Tetramethylbenzidine in Anionic and Cationic Micelles, J. Phys. Chem., 97, 5177 - 5184 (1993).

8. Conference and Seminar Presentations

1. (DOE-T369) Electron Spin Echo Modulation Studies of Nitroxide Probes in AOT Reversed Micellar Solutions, P. Baglioni, H. Nakamura and L. Kevan, 8th International Symposium on Surfactants in Solution, Gainesville, Florida, June 10-15, 1990.
2. (DOE-370) Photoionization of Alkylphenothiazine Sulfonates in Reversed Micelles, M. Hu and L. Kevan, American Society for Photobiology Annual Meeting, Vancouver, Canada, June 16-20, 1990.
3. (DOE-371) Photoinduced Charge Separation Across Surfactant Interfaces of Micelles and Vesicles, Plenary Lecture, L. Kevan, VIIIth International Symposium on Radiation Chemistry, Toluca, Mexico, July 9-13, 1990.
4. (DOE-372) Photoionization of Alkylphenothiazine Sulfonates in Reversed Micelles: Effects of Cosurfactants and Location of Chromophore, M. Hu and L. Kevan, Eighth International Conference on Photochemical Conversion and Storage of Solar Energy, Palermo, Italy, July 15-20, 1990.
5. (DOE-373) Contribution of Continuous and Pulsed Electron Spin Resonance to the Study of the Structure of the Interface of Sodium Dodecylsulfate and Dodecyltrimethylammonium Bromide Micellar Solutions with Added Urea, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, 11th IUPAC Conference on Chemical Thermodynamics, Como, Italy, August 26-31, 1990.
6. (DOE-374) Electron Spin Echo Modulation and Electron Spin Resonance Studies of the Effects of Urea Addition to Micellar Solutions, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, Fourth Conference on Trends in Colloid and Interface Science, Catanzaro, Italy, September 24-27, 1990.
7. (DOE-375) Electron Spin Echo Modulation and Electron Spin Resonance Studies of Anionic and Cationic Micellar Solutions: Effect of Urea Addition, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, XXIV National Congress on Chemical Physics, Potenza, Italy, October 8-12, 1990.
8. (DOE-T376) Electron Spin Echo Spectroscopy, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.

9. (DOE-T377) Two Pulse Electron Spin Echo Modulation, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.
10. (DOE-T378) Three Pulse Electron Spin Echo Modulation, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.
11. (DOE-T379) Applications of Electron Spin Echo Spectroscopy to Location Control of Electron Donors In Photoinduced Charge Separation Across Vesicle, Micelle and Reverse Micelle Interfaces, Invited Lecture, L. Kevan, 4th Chianti Workshop on Magnetic Resonance, San Minato, Italy, June 2-8, 1991.
12. (DOE-T380) Continuous and Pulsed-Wave ESR of Langmuir-Blodgett Films of Doxyl Stearic Acid, F. Bonosi, L. Kevan, G. Martini and M. Romanelli, 4th Chianti Workshop on Magnetic Resonance, San Minato, Italy, June 2-8, 1991.
13. (DOE-T381) Electron Spin Echo Modulation Study of Mixed Micelles of SDS, DTAC and Polyethylene Oxide Surfactants, P. Baglioni, E. Rivara-Minten and L. Kevan, American Chemical Society Colloid and Surface Chemistry Summer Symposium, Norman, Oklahoma, June 17-21, 1991.
14. (DOE-T382) Photoionization Near Vesicle, Micelle and Reverse Micelle Interfaces, Invited Lecture, 9th International Congress on Radiation Research, Toronto, Canada, July 7-12, 1991.
15. (DOE-T383) Applications of Electron Spin Echo Spectroscopy to Location Control of Electron Donors in Photoinduced Charge Separation Across Vesicle, Micelle and Reverse Micelle Interfaces, Invited Lecture, L. Kevan, Oji International Conference on Spin Chemistry, Tomakomai, Japan, July 15-18, 1991.
16. (DOE-T384) Photoionization of Neutral and Positively Charged Alkylphenothiazines in Positive, Neutral and Negatively Charged Vesicles: Effects of the Alkyl Chain Length, P. Bratt, Y.S. Kang and L. Kevan, 14th International EPR Symposium, Denver, Colorado, July 29 - August 1, 1991.

17. (DOE-T385) Photoreduction of Alkylmethylviologens in Vesicle Solution: Combined Effects of the Alkyl Chain Length in Alkylmethylviologen and the Addition of Cholesterol, M. Sakaguchi and L. Kevan, 44th Meeting of Colloid and Surface Science, Saitama University, Urawa, Japan, September 27-29, 1991.
18. (DOE-T386) Applications of Electron Spin Echo Modulation Spectroscopy, L. Kevan, Seminar, Institute for Physics Research, Rio de Janeiro, Brazil, February 21, 1992.
19. (DOE-T387) Photoreduction of Methylviologen In Organized Molecular Assemblies: Role of the Surfactant Headgroup, H.J.D. McManus, Y.S. Kang and L. Kevan, 203rd American Chemical Society National Meeting, San Francisco, California, April 5-10, 1992.
20. (DOE-T388) Photoreduction of Methylviologen in Organized Molecular Assemblies: Role of the Surfactant Headgroup, H.J.D. McManus, Y.S. Kang and L. Kevan, 16th DOE Solar Photochemistry Research Conference, Delavan, Wisconsin, May 31 - June 4, 1992.
21. (DOE-T389) Solvent Effects in Micellar Systems, P. Baglioni and L. Kevan, Invited Lecture, Ninth International Symposium on Surfactants in Solution, Varna, Bulgaria, June 10 - 15, 1992.
22. (DOE-T390) Electron Spin Echo Modulation and Small-Angle Neutron Scattering Studies of Lithium Dodecylsulfate Micellar Solutions: Effect of Lithium Encapsulation by the Macrocyclic Cage 5, 12, 17 Trimethyl-1, 5, 9, 12, 17-Pentaazabicyclo[7.5.5] nonadecane, P. Baglioni, S. H. Chen and L. Kevan, 66th Colloid and Surface Science Symposium, Morgantown, West Virginia, June 14 - 17, 1992.
23. (DOE-T391) Photoionization of N, N, N', N'-Tetramethylbenzidine Trapped in Sol-Gel Synthesized Silica, B. Xiang and L. Kevan, VI International Symposium on Magnetic Resonance in Colloid and Interface Science, Florence, Italy, June 22 - 26, 1992.
24. (DOE-T392) Electron Spin Echo Modulation and Small-Angle Neutron Scattering Studies of Lithium Dodecylsulfate Micellar Solutions: Effect of Lithium Encapsulation by the Macrocyclic Cage 5, 11, 12 Trimethyl-1, 5, 9, 12, 17-Pentaazabicyclo[7.5.5] nonadecane, P. Baglioni, S. H. Chen and L. Kevan, VI International Symposium on Magnetic Resonance in Colloid and Interface Science, Florence, Italy, June 22 - 26, 1992.

25. (DOE-T393) Electron Spin Echo Modulation of Nonionic Surfactant Micellar Solutions in the Presence of Urea: Evidence for Urea Interaction at the Micellar Surface, P. Baglioni, L. Dei, P. Lo Nostro and L. Kevan, 204th American Chemical Society National Meeting, Washington, D.C., August 24 -28, 1992.
26. (DOE-T394) Subpicosecond Solvation Dynamics In Micelles, P. Baglioni, P. Foggi, R. Righini and L. Kevan, 204th American Chemical Society National Meeting, Washington, D.C., August 24 - 28, 1992.
27. (DOE-T395) The Complementarity of Electron Spin Echo Deuterium Modulation and Proton Matrix Electron Nuclear Double Resonance for Probing the Surroundings of Photoproduced Radical Ions in Disordered Systems of Frozen Surfactant Assemblies, Y. S. Kang, H.J.D. McManus and L. Kevan, XXVI Congress Ampere on Magnetic Resonance, Athens, Greece, September, 6-12, 1992.
28. (DOE-T396) Comparative Electron Magnetic Resonance, Electron Spin Echo Modulation and Electron Nuclear Double Resonance Studies of Photoinduced Electron Transfer from N-Alkylphenothiazines Across Micelle and Vesicle Interfaces, Y.S. Kang, H.J.D. McManus and L. Kevan, Third Eurasia Conference on Chemical Science, Bangkok, Thailand, December 14-18, 1992.
29. (DOE-T397) Charge Separation in Photoredox Systems, L. Kevan, Solar Photochemistry Research Program Review, Bethesda, Maryland, January 28, 1993.
30. (DOE-T398) Light Energy Storage in Model Membranes, Larry Kevan, Welch Lectureship, Mary Hardin-Baylor University, Belton, Texas, April 12, 1993.
31. (DOE-T399) Light Energy Storage in Model Membranes, Larry Kevan, Welch Lectureship, Southwestern University, Georgetown, Texas, April 13, 1993.
32. (DOE-T400) Light Energy Storage in Model Membranes, Larry Kevan, Welch Lectureship, Pan American University, Edinburg, Texas, April 14, 1993.
33. (DOE-T401) Light Energy Storage in Model Membranes, Larry Kevan, Seminar, National University of Mexico, Mexico City, Mexico, May 18, 1993.

34. (DOE-T402) Photoinduced Charge Separation Across Vesicle and Micelle Interfaces, L. Kevan, Invited Lecture, 17th DOE Solar Photochemistry Research Conference, Brainerd, Minnesota, June 6-10, 1993.