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Pulsed Electron Paramagnetic Resonance Application on the Photoinduced Charge Separation of Alkylphenothiazine Derivatives in Molecular Assemblies

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Abstract: Photoinduced charge separation of alkylphenothiazines in molecular assemblies such as positively, negatively and neutrally charged micelle interface results in the paramagnetic phenothiazine cation radical. This was studied as a model system for the light energy conversion into chemical energy. The photoproduced phenothaizne cation radical was identified and its amount was quantized with electron spin resonance (ESR). The microenvironment of photoproduced cation radical was studied with pulsed-ESR. Such a charge separation is enhanced by the optimization of various structural factors of the molecular assemblies. The structural factors of molecular assemblies have focused on the interface charge, interface structure with different headgroups and interfacial perturbation by disolving interface active organic additives.

INTRODUCTION

Recently much attention has been focused on the conversion of light energy into chemical or electrical energy.[1-3] Efficient storage and conversion of solar energy provide an almost limitless and renewable energy source. Many attempts have been made to simulate the naturally occurring photosynthesis of chlorophyll a in a biomembrane.[4-6] Photosynthesis, the process by which light from the sun is converted into the energy necessary for the vital functions of living matter, the keystone of life on earth. The main process of photosynthesis is the conversion of light energy into chemical energy by absorption of quanta of light energy and its storage by net charge separation of photosensitive materials within a biomembrane. During the charge separation process, an electron donor or electron acceptor (or both) are changed to their excited state to give or accept an electron from their counterparts. For efficient charge separation of photosensitive chromophores, organized molecular assemblies, such as micelles, reverse micelles and vesicles, are commonly used as model systems for artificial photosynthesis.[3,7] For the effective charge separation in surfactant aggregates, some general conditions should be satisfied for the photosensitive electron donors and acceptors. The conditions are such as low ionization potential of

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photosensitive molecules, low reactivity of photosensitive molecules in organic or aqueous environments, relatively simple optical absorption spectrum and location control of the chromophore. Also the micelles as organized molecular assembly are found to enhance the photoionization yield. This can be controlled by the chemical structure of headgroups and inteface charge.[4,8]

Normally, analysis of the electron spin resonance (ESR) spectrum of a paramagnetic species can give information on the identification of the species, together with its geometrical and electronic structure, and the environment of the radical.[9] In the present study, ESR is used to identify the photoproduced paramagnetic cation radical and to determine its relative concentration. A kind of pulsed ESR, electron spin echo modulation (ESEM), can be used to obtain information on the structure of the surrounding nuclear environment. ESEM has been used extremely useful for the determination of the solvation structure and the number, distance and orientation of molecules in the local environment around a paramagnetic species, particularly in disordered systems.[10] The location control of the phenothiazine chromophore in micelles as a function of the attached pendant alkyl chain length and the nature of the surfactant are studied here by measuring the deuterium modulation depth by ESEM in deuterium oxide surfactant suspensions.

In this study, N-alkylphenothiazines were used to penetrate more deeply into a micelle. The photoionization efficiency was determined by electron spin resonance (ESR) and the penetration degree into the micellar core was determined by electron spin echo modulation (ESEM) spectroscopy.

EXPERIMENTAL SECTION

Five N-alkylphenothiazines were synthesized by using a modified literature procedure.[11] Sodium decyl sulfate ($NaC_{10}SO_4$) was obtained from Eastman Kodak; Sodium dodecyl sulfate ($NaC_{12}SO_4$) and sodium tetradecyl sulfate ($NaC_{14}SO_4$) were obtained from Aldrich and used after recrystallization. Decyltrimethylammonium bromide (C_{10}(TAB), Eastman Kodak) and both dodecyl- and tetradecyltrimethylammonium bromide (C_{12}(TAB) and C_{14}(TAB), Aldrich) were recrystallized three times from acetone and dried under a moderate vacuum. Stock solutions of 0.1 M surfactant were prepared in deuterium oxide. The deuterium oxide was first deoxygenated by purging with dry nitrogen gas for 15 min. For each alkylphenothiazine, 2.5×10^{-4} mol were added to 25 ml of chloroform. The concentration of each of the solutions were checked by using UV/vis spectroscopy (λ_{max} = 320 nm ; log ε = 3.71 $M^{-1}cm^{-1}$) and was determined to be 1×10^{-2} M. A 40 μl quantity of each N-alkylphenothiazine stock solution was transferred into a 2–mL vial. The chloroform was then evaporated by gas onto the surface of the solution, which resulted in the formation of a thin film of N-alkylphenothiazine on the wall of the sample vial. One milliliter of the 0.1 M micellar stock solution was then added mixture for 5 min. The sample were then sonicated with a Fisher Model sonic dismembrator operated at 35% relative output with a 4-mm-o.d.

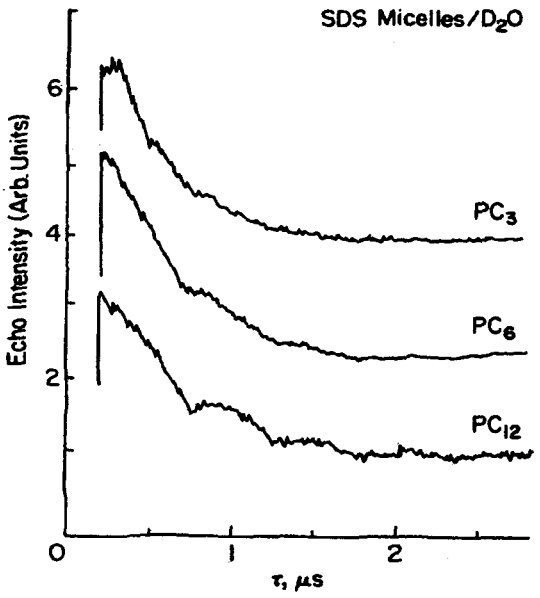

Fig. 1. Two-pulse ESE signals at 4.2 K of photoionized PC_3, PC_6 and PC_{12} solubilized in sodium dodecyl sulfate micelles. The signals are offset vertically

microtip under nitrogen gas flow at 58±3 °C for 5 min. Clear solution were obtained, which indicated complete solubilization of N-alkylphenothiazines. The samples were then placed in 2-mm-i.d. x 3-mm-o.d. Suprasil quartz tubes that were sealed at one end. The samples were frozen by rapidly plunging the quartz cells into liquid nitrogen. Photoirradiation of the frozen N-alkylphenothiazines samples was carried out at 77 K for 10 min with a 300-W xenon lamp (ILC-LX 300 UV). A 10-cm water filter and a corning No.7-54 filter (70% transmittance at 310 nm) were placed in a light path. The Dewar holding the ESR cell was rotated during irradiation to ensure even irradiation of the sample. ESR spectra were recorded at 77 K on a Bruker ESP 300 ESR X-band spectrometer. Each ESR spectra was scanned four times. The photolysis yield of the N-alkylphenothiazine was then determined by double integration of the ESR spectrum. Each phototolysis was normalized to the yield for N-dodecylphenothiazine solubilized in the decyltrimethylammonium bromide micellar solution. Two-pulse electron spin echo deuterium modulation signals were recorded at 4.2 K on a home-built spectrometer using 40-ns excitation pulses. The deuterium modulation depths were normalized by dividing the depth at the first modulation minimum from an extrapolated unmodulated echo decay by the depth to the baseline at that interpulse time.

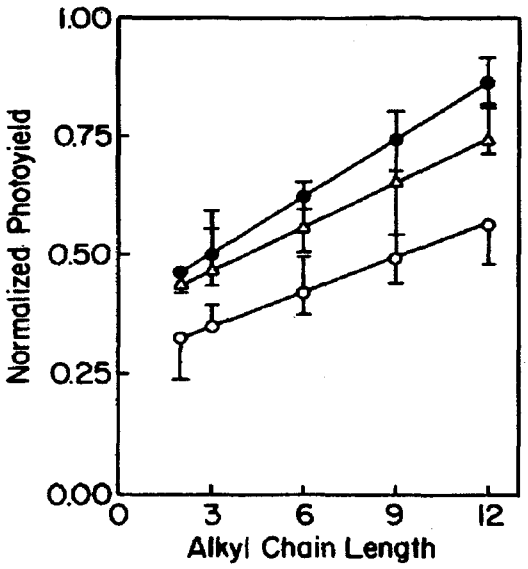

Fig. 2. Normalized PC_n photocation yield, measured by ESR at 77 K, as a function of PC_n alkyl chain length for sodium alkyl sulfate micelles. Error bars indicate the standard deviation (● = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates)

RESULTS AND DISCUSSION

Two-pulse ESE decay signals at 4.2 K for three N-alkylphenothiazine radical cations solubilized in SDS micelles showed a modulation with a 460-ns period as Fig. 1, characteristic of the deuterium Lamor precession in a 3.3-kG magnetic field. The photoyield data at 77 K for the PC_n^+ cations in sodium alkyl sulfate micellar solutions versus PC_n alkyl chain length are given in Fig. 2. Fig. 3 shows the normalized ESE deuterium modulation depths for PC_n^+ cations in sodium alkyl sulfate micellar solutions as a function of PC_n chain length. Fig. 4 shows the photoyield at 77 K of PC_n^+ cations versus alkyl chain length for three alkyltrimethylammonium bromide micellar systems. The normalizerd deuterium modulation depths for these systems are plotted in Fig. 5. The photoyield of N-alkylphenothiazine solubilized within a micelle is affected by the location of the molecules with respect to the interface, the structure of the micellar interface, and the energy barrier encountered by the photoejected electron. These factors are interrelated. The photoyield and ESEM data obtained in this study can be explained by the effects that the alkyl chain length has on the location of the phenothiazine moiety with respect to the micelle interface.

With photoirradiation, the phenothiazine moiety is ionized with the electron ejected into the bulk water (D_2O) phase to give a phenothiazine cation radical (PC_n^+).[12] The g-factor

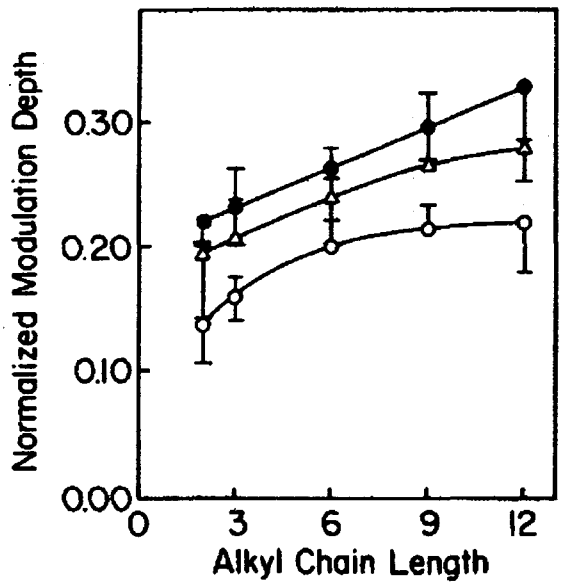

Fig. 3. Normalized deuterium modulation depth at 4.2 K as a function of PC_n alkyl chain length in micellar solutions of sodium alkyl sulfates (● = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates)

of the ESR singlet formed is 2.0052. This assignment is consistent with the g-factors reported for cation radicals of alkylphenothiazine derivatives such as g = 2.0052 for ethylphenothiazine and methylphenothiazine,[13] g = 2.0053 for phenothiazine,[14] and g 2.0059 for propylphenothiazinesulfonate.[15]

The photoyield data of these N-alkylphenothiazine derivative cations display several trends in Fig. 2 and 4. First, the photoyield increases monotonically with the increasing alkyl chain length of the alkylphenothiazine. Second, the radical yield decreases as the alkyl chain length of the surfactant molecule forming the micelles is increased. Finally, when comparing the photoyield of a particular N-alkylphenothiazine in cationic versus anionic frozen micelle solutions, the yield is consistently larger in the cationic micelles as has been found for other photoionizable solutes.[16] This is consistent with a lower energy barrier at the interface for the escape of a photoejected electron from a cationic micelle than from an anionic micelle.

The change in the cationic photoyield with cation and surfactant alkyl chain length can be explained by an analysis of the electron spin echo modulation data. The ESEM data also display several trends in Fig. 3 and 5. The normalized deuterium modulation depths increase with increasing alkyl chain length of the cation. Also the normalized modulation

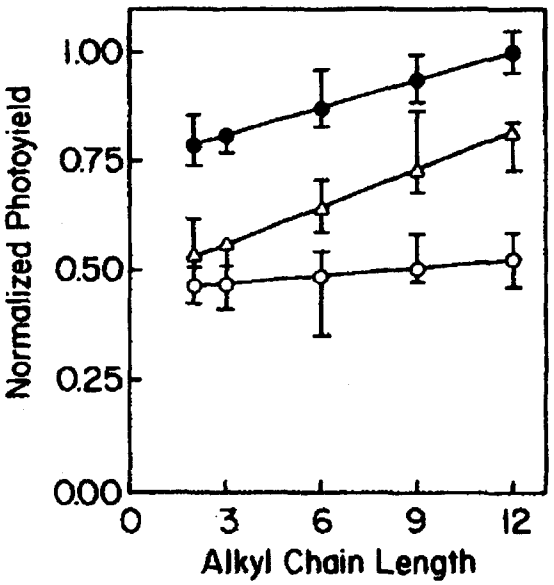

Fig. 4. Normalized PC_n photoyield, measured by ESR at 77 K, as a function of PC_n alkyl chain length in micellar solutions of alkyltrimethylammonium bromides (● = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates)

depth decreases as the surfactant alkyl chain length increases. This modulation of the spin-echo signal results from weak, dipolar hyperfine interaction of the unpaired electron with nearby magnetic nuclei. The modulation depth increases with an increase in the number of interacting nuclei and decreases as the mean interaction distance increases. The trend displayed in Fig. 3 and 5 of increasing modulation depth with increasing alkyl chain length on the alkylphenothiazines can be explained by movement of the phenothiazine moiety from the micellar interior toward the interface region where it interact more strongly with water (D_2O). As the alkyl chain lengthens and the phenothiazine moves toward the interface, the photolysis yield also increases as expected. These two observations indicate that the cation yield is correlated with the extent of interaction between the photoproduced cation and water and with the location of the cation with respect to the micellar interface. As the length of the surfactant alkyl chain increases, the normalized deuterium modulation depth and the photoyield for a given N-alkylphenothiazine both decrease in the order $C_{10} > C_{12} > C_{14}$. For a micelle composed of sodium decyl sulfate monomers, one expects a more open headgroup region compared to either dodecyl sulfate or tetradecyl sulfate. This more open interface is caused by a smaller aggregation number for decyl ($N_o = 50$) than either dodecyl ($N_o = 62$) or tetradecyl ($N_o = 118$) sulfate.[18] A more open interface results in greater water penetration

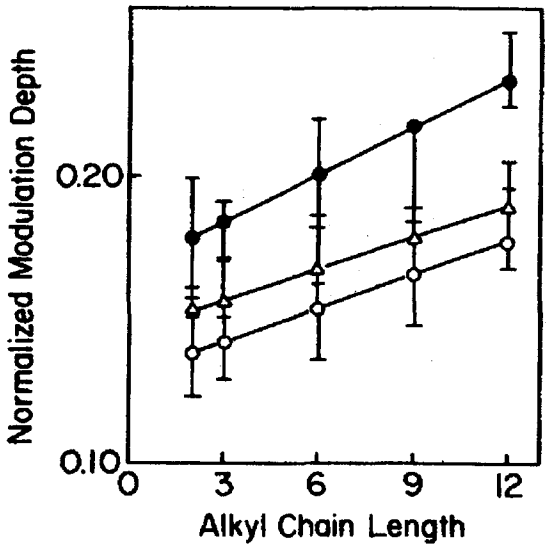

Fig. 5. Normalized deuterium modulation depth at 4.2 K as a function of PC_n alkyl chain length in micellar solutions of alkyltrimethylammonium bromides (● = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates)

nto the micellar interface. These points explain why the deuterium modulation depth observed for the sodium decyl sulfate is consistently greater than for either the decyl or tetradecyl sulfate micellar systems.

The deuterium modulation depth depends on the number of interacting magnetic nuclei and upon the mean distance of the paramagnetic species from those nuclei; therefore, the decrease in the deuterium modulation depth results from a decrease in the number of water (D_2O) molecules in the interface region or an increase in the mean distance from the deuterium nuclei in the interface. Since both the normalized modulation depth and the photoyield of a given N-alkylphenothiazine increases as the alkyl chain length of the micellar surfactant decreases, the photoionization efficiency correlates with the extent of interaction between the water and the photoproduced cation.

CONCLUSIONS

The results obtained from the analysis of the electron spin resonance spectra and the electron spin echo modulation patterns of photogenerated cations of phenothiazine derivatives solubilized in sodium decyl, dodecyl, and tetradceyl sulfate and in decyl-, dodecyl, tetradecyltrimethylammonium bromide micellar solutions show that the photoyield

of the cation generally correlates with the deuterium modulation depth. The photolysis yield and the normalized deuterium modulation depth increase as the alkyl chain on the phenothiazine is lengthened, and decrease as the micelle surfactant chain length is increased. These observations support the conclusion that the photoyield is related to the strength of photoproduced cation-water interactions and the location of the phenothiazine moiety is near the micellar interface. Phenothiazines solubilized in anionic micellar systems show a larger deuterium modulation depth compared with those solubilized in analogous cationic micelles. The photoyields are slightly larger in cationic micelles versus anionic ones. This increase is attributed to a lower energy barrier for a photoejected electron to traverse a cationic micelle interface. Micelles formed from shorter chain surfactants have more water penetration at the interface compared to micelles formed from longer chain surfactants. This is supported by an increase in the normalized deuterium modulation depth with a decrease in the micelle surfactant chain length.

Acknowledgments

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