Photoinduced Electron Transfer from N-Alkylphenothiazines to Interface Water of Sodium Dodecyl Sulfate Micelles as a Function of Poly(ethylene oxide) Interaction with the Interface

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Photoinduced electron transfer from N-alkylphenothiazines (PC_n, n = 1, 3, 6, 12, and 16) solubilized in sodium dodecyl sulfate (SDS) micelle interacting with poly(ethylene oxide) (PEO) to interface D_2O as an electron acceptor is studied with electron spin resonance (ESR) and electron spin echo modulation. The photoproduced radicals are identified as the N-alkylphenothiazine cation radical and the surfactant alkyl chain radical of SDS. The total photoyield decreased from PC_1 to PC_3 and then increased to PC_{16}. The photoyields increased monotonically with increasing PEO concentration. The photoyields are correlated with the deuterium modulation depth of PC_n^+ with D_2O at the micelle interface as a function of the alkyl chain length of PC_n and the concentration of PEO since the modulation depth measures relative changes in the interaction distance between the phenothiazine moiety and interface D_2O. The photoyield and deuterium modulation depth trends show a good correlation which indicates that the electron transfer from phenothiazine moiety to interface water is mainly controlled by the distance between them, which is controllably varied by the alkyl chain length of phenothiazine and the intercalation of PEO into the interface region of the SDS micellar headgroup.

Introduction

Molecular assemblies such as micelles, vesicles, and reverse micelles are being explored as artificial photosynthetic model systems.[1-4] Such molecular assemblies allow compartmentalization of electron donors and acceptors relative to the solvent external to the interface, which is usually water. Photoinduced net charge separation can be partially controlled by variation of several aspects of the molecular assembly such as interface charge,[5-9] headgroup variation,[5,8] alkyl chain length variation,[5,10] and addition of slightly water-soluble molecules like alcohols, urea, and cholesterol, which modify the assembly interface.[11-15]

A photoproduced cation radical is paramagnetic so it can be monitored by electron spin resonance (ESR) for identification and quantitation. Electron spin echo modulation (ESEM) spectroscopy can also be applied to determine structural information about the location of the cation radical within the surfactant assembly, especially with respect to the interface.[4] This has led to a general correlation between the net photoionization yield and the strength of the photoproduced cation interaction with deuterated water at the assembly interface as measured by the deuterium modulation depth determined by ESEM spectroscopy.

Such ESR and ESEM studies are carried out in the frozen state to stabilize the photoproduced radical cations for quantitation and to exploit ESEM to measure weak dipolar interactions which are averaged out in liquid solution.[16-18] Numerous studies have demonstrated that micellar and vesicular structure is retained in rapidly frozen aqueous solution,[19a] and recent work has demonstrated similar structural characteristics of nitroxide spin probes in liquid and frozen vesicle systems.[19b,c]

In the present study, the effect of poly(ethylene oxide) (PEO) interaction with a sodium dodecyl sulfate (SDS) micelle interface on the photoionization of N-alkylphenothiazines (PC_n with n = 1, 3, 6, 12, 16) has been studied. The variable alkyl chain length of PC_n changes the distance from the phenothiazine moiety and the micelle interface. PEO perturbs the micellar interface to affect the efficiency of electron transfer through it.

Experimental Section

Sample Preparation. N-Alkylphenothiazines (PC_n) were synthesized by the modified synthetic procedures described previously.[20] Stock solutions of the PC_n samples were prepared in chloroform. The exact concentration was measured with optical absorption spectroscopy using a Perkin-Elmer 330 spectrophotometer (λ_{max} = 312 nm in chloroform, log ϵ = 3.71 M^{-1} cm^{-1}).[21] Deuterium oxide (D_2O) was purchased from Aldrich Chemical Co. (99.8 atom % D) and was deoxygenated by purging with nitrogen gas for 20 min before use. SDS surfactant was obtained from Eastman Kodak. This surfactant was recrystallized three times from ethanol and washed with ethyl ether, followed by drying at 50 °C under a moderate vacuum. PEO (99.9%, average molecular weight of 10 000) was obtained from Aldrich and used without further purification. Stock micellar solutions of 0.1 M SDS were prepared in deoxygenated deuterium oxide. Each SDS micellar solution of 0, 0.5, 1, 2, 4, and 10 mM concentration of PEO was prepared by dissolving 0, 5, 10, 20, 40, and 100 mg of PEO powder. Then 70 μL of each N-alkylphenothiazine stock solution was transferred into a 16- × 125-mm test tube. The solvent was evaporated under a stream of pure nitrogen which resulted in the formation of a thin film on the test tube wall. After the film had formed, 1 mL of each of the 0.1 M SDS micellar solutions in D_2O was added to the test tube. The resulting suspensions were sonicated for 5 min at 45 ± 3 °C with a Fisher Model 300 sonic dismembrator operated at 35% relative output power through a 4-mm-o.d. microtip under a nitrogen gas atmosphere to obtain a clear solution. The exact N-alkylphenothiazine concentration of the resulting micellar aqueous suspensions was measured as 6.02×10^{-4} M with optical absorption spectroscopy.

Photoirradiation and Data Acquisition. The samples for photolysis were prepared by taking 100 μL of each solution and transferring it into a 2-mm-i.d. × 3-mm-o.d. Suprasil quartz tube which was flame-sealed at one end. The tubes were shaken to equilibrate the solution, and then the samples were frozen by rapidly plunging into liquid nitrogen.

Photoirradiation of the ESR samples was carried out for 10 min at 77 K. Samples for ESEM experiments were irradiated for 5 min. The photolysis source used was a 300-W Cermax xenon lamp (CX 300 UV) with a power supply from ILC Technology. The light passed through a 10-cm water filter and a glass optical filter (Corning glass filter No. 7-54, 86% transmittance at 320 nm, 240 nm < λ < 410 nm). The Dewar holding the sample tube was rotated at 4 rpm during photolysis

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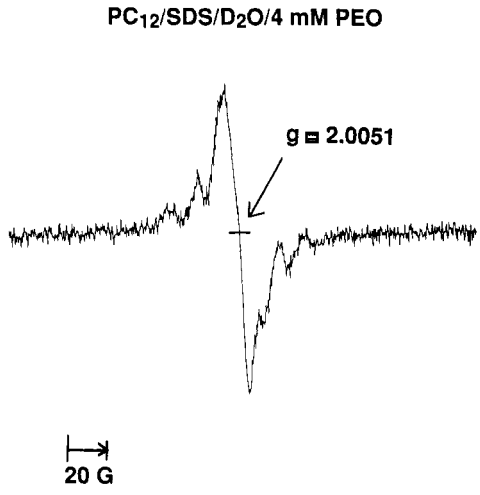

Figure 1. ESR signal at 77 K of PC_{12}^+ in SDS/D_2O micelles with 4 mM PEO after 10-min photoirradiation at 77 K.

to ensure even irradiation at the sample position. The light intensity was measured with a YSI-Kettering Model 65 radiometer as 1.1×10^{-3} W m^{-2}.

ESR spectra were recorded at X-band using a Bruker ESP 300 spectrometer with 100-kHz field modulation. The irradiated sample cell was placed in a quartz ESR Dewar (Wilmad Glass Co.) which was filled with liquid nitrogen and secured in a TE_{102} cavity. The loaded Q factor of this cavity was measured as about 1700. The microwave power was 1.97 mW. The microwave frequency was measured with a Hewlett-Packard 5350B frequency counter, and the magnetic field was monitored with a Bruker ER 032M Hall effect field controller. The standard ESR spectrometer settings were 0.28-mT field modulation amplitude, 10-mT sweep width, seven-scan accumulation, 56-s scan time constant, microwave frequency 9.495 GHz, and 1.25×10^5 receiver gain. The photoproduced radical yield was determined by double integration of the first-derivative ESR spectra using the ESP 1600 computer software. Each relative photoyield value is an average of triple determinations and is normalized by dividing by the photoyield of a $PC_{16}/SDS/D_2O$/10 mM PEO sample.

Two-pulse ESEM signals were recorded at 4.2 K on a home-built X-band ESE spectrometer using 40- and 80-ns excitation pulses.[22,23] The microwave frequency incident upon the sample was measured with a Hewlett-Packard 5342A microwave frequency counter, and the magnetic field was monitored with a Varian F501 gaussmeter. The microwave pulse sequence and data acquisition process were controlled by a Nicolet 12/80 minicomputer which was interfaced to the ESEM spectrometer. Once obtained, the ESEM data were transferred to an IBM-compatible 386 based microcomuter for later, off-line analysis. The deuterium modulation depths were normalized by dividing the depth at the first deuterium modulation minimum from an extrapolated, unmodulated echo decay by the depth to the base line at the same interpulse time.[12,24]

Results

Samples not containing *N*-alkylphenothiazines show no ESR signal after photoirradiation. Also, the samples before photoirradiation give no ESR signal. These results imply that *N*-alkylphenothiazine is the only photoionizable molecule in the samples studied. The pink color and the singlet ESR signal of PC_n^+ at $g = 2.0051$ are consistent with previous reports of phenothiazine cation radical.[20,25-30] A weaker background ESR signal due to the presence of an alkyl radical was also observed as shown in Figure 1. This species is produced by radical conversion from the phenothiazine cation to the surfactant alkyl chain and has been previously reported.[20,25-30]

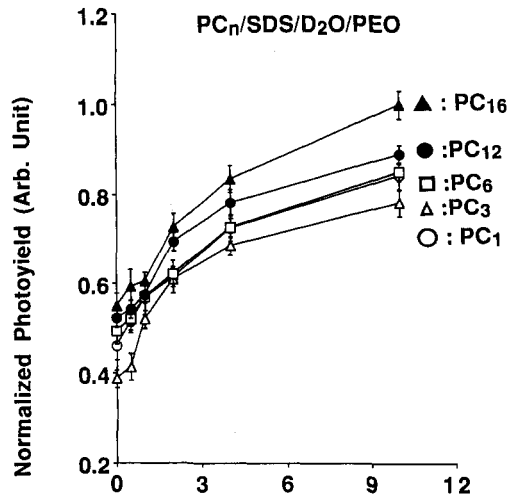

Figure 2. Normalized photoyields at 77 K of PC_n in SDS/D_2O micelles with 0 (○), 0.5 (△), 1 (□), 2 (●), 4 (▲), and 10 mM (■) PEO versus the alkyl chain length of PC_n after 10-min photoirradiation at 77 K.

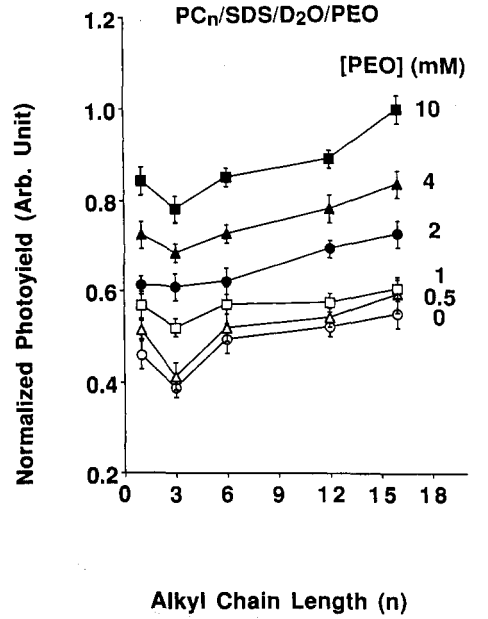

Figure 3. Normalized photoyields at 77 K of PC_1 (○), PC_3 (△), PC_6 (□), PC_9 (●), PC_{12} (▲), and PC_{16} (■) in SDS/D_2O micelles versus the concentration of PEO (mM) after 10-min photoirradiation at 77 K.

The normalized photoyields of PC_n versus the alkyl chain length of alkylphenothiazine in SDS micelles with each concentration of PEO are shown in Figure 2. The photoyield decreases from methyl to propyl chains and then increases up to the hexadecyl chain. The photoyields of PC_n increase versus the concentration of PEO as shown in Figure 3.

The ESEM signals of PC_3 in SDS/D_2O surfactant with each concentration of PEO are shown in Figure 4. Deuterium modulation with a 0.5-μs periodicity is observed. The normalized deuterium modulation depths of PC_n versus the alkyl chain length of PC_n in SDS/D_2O micelles with each concentration of PEO are shown in Figure 5. The normalized deuterium modulation depth decreases from PC_1 to PC_3 and then increases up to PC_{16}. The normalized deuterium modulation depths of PC_n versus the concentration of PEO in SDS/D_2O micelles are shown in Figure 5. The deuterium modulation depth increases monotonically to 4 mM and is then constant up to 10 mM.

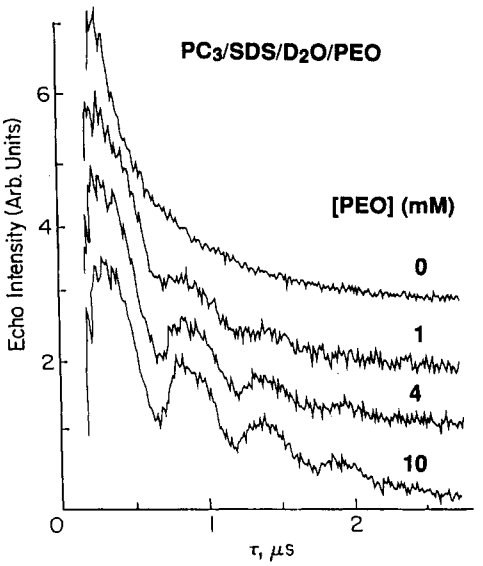

Figure 4. Two-pulse ESEM signals at 4.2 K of PC_3^+ in SDS/D_2O micelles with increasing concentration of PEO from 0 to 10 mM after 5-min photoirradiation.

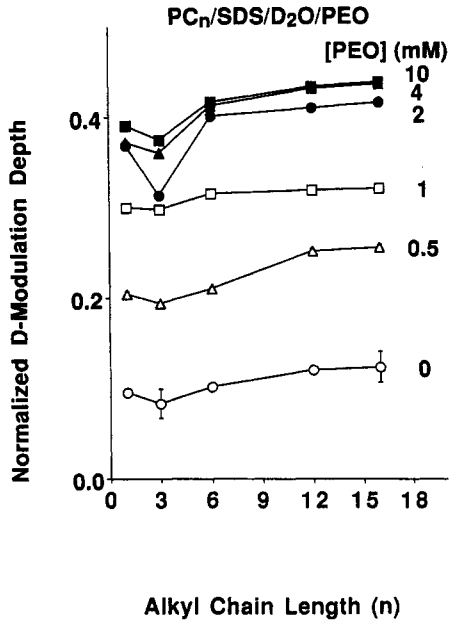

Figure 5. Normalized deuterium modulation depths at 4.2 K of PC_n^+ in SDS/D_2O micelles with 0 (○), 0.5 (△), 1 (□), 2 (●), 4 (▲), and 10 mM (■) PEO versus the alkyl chain length of PC_n after 5-min photoirradiation at 77 K.

Discussion

ESR spectra of the photoirradiated samples showed two radicals. The broad singlet at $g = 2.0051$ is identified as a photoproduced alkylphenothiazine cation radical. This is consistent with $g = 2.0052$ for *N*-ethylphenothiazine,[31] $g = 2.0053$ for *N*-methylphenothiazine,[32] $g = 2.0053$ for 10*H*-phenothiazine,[33] and $g = 2.0053$ for 2-methoxyphenothiazine.[34] Also, each photoirradiated sample shows a pink color which is characteristic of alkylphenothiazine cation radicals.[35,36] A secondary radical was also observed. This species is a surfactant secondary alkyl radical which has been previously reported.[25-30] The secondary radical is formed from phenothiazine cation radical by abstraction of a hydrogen from the surfactant alkyl chain followed by migration of the radical site to the penultimate carbon.

The radical conversion was enhanced by prolonged irradiation of the samples. The intensity of the phenothiazine cation radical decreased as a function of the irradiation time, whereas the intensity of the secondary radical increased. Further, the pink color of the irradiated sample faded with prolonged photolysis.

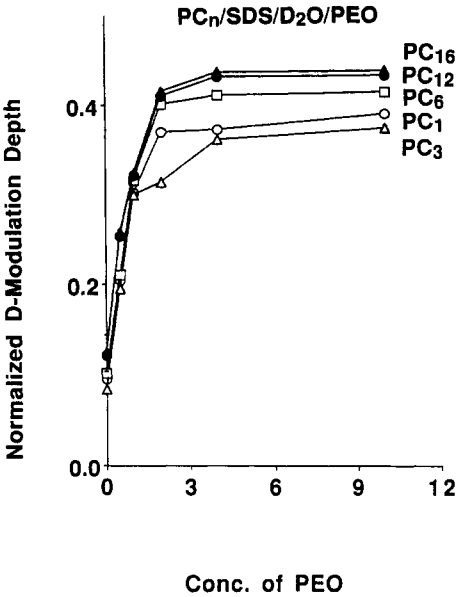

Figure 6. Normalized deuterium modulation depths at 4.2 K of PC_1 (○), PC_3 (△), PC_6 (□), PC_9 (●), PC_{12} (▲), and PC_{16} (■) in SDS/D_2O micelles versus the concentration of PEO (mM) after 5-min photoirradiation at 77 K.

Effect of Alkyl Chain Length. The electron-transfer distance in the frozen SDS micelles is the distance between the phenothiazine moiety and interface water as the acceptor. This is modified by the alkyl chain length of PC_n as shown by the change in the deuterium modulation depth from interface D_2O in Figure 5. A greater modulation depth indicates a shorter electron-transfer distance. The increasing alkyl chain length of PC_n from methyl to propyl chains increases the electron-transfer distance because of increasing hydrophobic interaction of PC_n with SDS surfactant alkyl chains, but this is reversed from propyl to hexadecyl chain lengths due to steric interactions between the alkylphenothiazine and the highly disordered surfactant alkyl chains. The changes in electron-transfer distance correlate well with the changes in photoionization yield shown in Figure 2. This is consistent with previous work on the photoionization of alkylphenothiazines[20] and alkyltrimethylbenzidines[36] in micelles.

Effect of PEO Addition. The electron-transfer distance is also modified by addition of PEO to the SDS micellar interface. This is a much larger effect than the alkyl chain length effect as can be seen by comparing Figures 5 and 6. The PEO intercalates between the surfactant headgroups to allow more water penetration into the interface region, which decreases the distance between interface water and the phenothiazine moiety. So, PEO addition to SDS micelles increases the photoyield of PC_n as shown in Figure 2. The constant deuterium modulation depth from 4 to 10 mM PEO can be explained by partial cancellation of the intercalation effect of PEO into the interface region of the SDS micelle by replacement of some interface water by PEO at higher PEO concentrations. This agrees with similar results on the photoyield and the deuterium modulation depth of tetramethylbenzidine photoionization in SDS micelles with alcohol addition[11] and of alkylphenothiazine photoionization in SDS micelles with urea addition.[14]

In addition to the decrease of the electron-transfer distance, PEO addition decreases the anionic interface charge density of SDS micelles by intercalation between the micellar headgroups. This also contributes to increasing the photoyield of PC_n by decreasing the energy barrier for electron transfer through the interface. This is further supported by the increasing photoyields of PC_n from 4 to 10 mM PEO while the deuterium modulation depth of PC_n remains constant above 4 mM PEO. At higher

concentrations of PEO the electron-transfer distance remains constant, but the energy barrier for electron transfer decreases. This explains the observed data on both the photoyields and the deuterium modulation depths.

Conclusions

The photoyield of PC_n in SDS micelles is increased with the alkyl chain length of PC_n and with PEO addition, with the effect being greater for PEO. The increasing alkyl chain length initially decreases the photoyield for methyl to propyl chains due to a longer interaction distance between the phenothiazine moiety and interface water by increasing the hydrophobic interaction of PC_n with the surfactant alkyl chains. But for longer alkyl chains the photoyield increases up to hexadecyl chain lengths because steric factors inhibit penetration of PC_n into the disordered SDS micelle and decrease the electron-transfer distance. PEO increases the photoyield by intercalating into the micellear interface to increase water penetration into the interface and decrease the electron-transfer distance. PEO also decreases the anionic charge density of the interface of SDS micelles, which decreases the energy barrier for electron transfer through the interface.

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