Electron Spin Resonance and Electron Spin Echo Modulation Studies on Photoinduced Charge Separation from *N*-Alkylphenothiazines in Sodium Dodecyl Sulfate Micelles: Effect of α- and β-Cyclodextrin Addition

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Photoinduced electron transfer from *N*-alkylphenothiazines (PC_n, $n = 3, 9, 12, 16$) to D_2O at a micellar interface was monitored versus the alkyl chain length of PC_n and versus cyclodextrin (CD) addition into the micelle by determining the photoproduced radical yield by electron spin resonance. The photoyield of PC_n in sodium dodecyl sulfate micelles monotonically decreases with increasing concentration of α-CD. This results from an increased electron transfer distance between the phenothiazine moiety and interface D_2O by replacing some interface D_2O with α-CD. Addition of β-CD shows a different trend for the photoyield. The photoyield increases with increasing concentration of β-CD up to 10 mM and thereafter monotonically decreases. The increased photoyields up to 10 mM β-CD result from a decreased interaction distance between the phenothiazine moeity and D_2O at the micellar interface by intercalation of β-CD between the headgroups of the surfactant molecules. The decrease of photoyield above 10 mM β-CD results from an initial increased interaction distance between the phenothiazine moiety and interface water by replacing some D_2O at the micellar interface to 15 mM β-CD and thereafter disrupting the micellar structure by the high concentration of β-CD.

Introduction

Photoinduced charge separation in molecular assemblies such as micelles, reverse micelles, and vesicles is one model system for light energy conversion into chemical energy and its storage.[1−5] The photoinduced electron transfer yield is given by the net photoproduced radical yields.[4,5] This is controlled by several factors. Two critical parameters are the electron transfer distance and the energy barrier for electron transfer through the interface of the molecular assemblies. The distance can be changed by relative location control of the electron donor and acceptor. The energy barrier can be modified by perturbing the interface structure and by changing the interface charge.

In molecular assemblies the electron transfer distance from electron donors within molecular assemblies to an electron acceptor at the assembly interface can be modified by changing the pendant alkyl chain length of the electron donor because different alkyl chain lengths have different degrees of hydrophobic interaction with the surfactant alkyl chains forming the assembly. In previous studies the location of the photosensitive moiety of electron donors such as porphyrins,[6,7] phenothiazines,[8−10] and benzidines[11,12] and of electron acceptors such as viologens[13,14] was controlled relative to the assembly interface by changing their pendant alkyl chain lengths and by perturbing the interface structure of the molecular assemblies. The interface structure was modified by adding surface active molecules into the molecular assemblies. The intercalation of the surface active molecules such as alcohol,[15] crown-ether,[16] and urea and its derivatives[17,18] between the headgroups of the surfactants results in a decreased interaction distance between the electron donor and the electron acceptor.

The electron transfer efficiency can be monitored by double integration of the electron spin resonance (ESR) spectra of the photoproduced cation radicals and their reaction product radicals if any. The photoyield is compared with interaction distance changes between the donor and bulk water as an electron acceptor at the surfactant assembly interface. The interaction distance changes can be measured with deuterium electron spin echo modulation (ESEM)[4,19,20] from deuterated water at the interface.

Cyclodextrins (CDs) have been used as complexation materials for a variety of organic guests. The CDs are cyclic, nonreducing oligosaccharides built from six, seven, or eight glucopyranose units. CDs are water soluble since all of the free hydroxyl groups are on the outer surface of the ring. The internal cavity of the doughnut-shaped molecules is slightly apolar and allows hydrophobic interaction with organic hydrocarbons.[21,22] This forms inclusion complexes with hydrophobic organic compounds including surfactants.[23−27] The interaction of CDs with surfactants below or near the critical micellar concentration greatly affects the physical properties of the surfactants.

In the present study, the effect of CD addition on the photoionization of *N*-alkylphenothiazines (PC_n, $n = 3, 9, 12, 16$) in sodium dodecyl sulfate (SDS) micelles is studied. α- and β-CDs are used to perturb the interfacial structure of the micelles. The perturbation changes the interface water structure and the electron transfer distance from the phenothiazine moiety to the interface water. Alkylphenothiazine cation radical photoyields were determined by ESR spectra double integration and correlated with the distance changes of the cation radical from interface water determined by ESEM from D_2O at the interface.

Experimental Section

Materials. Sodium dodecyl sulfate, α-CD, and β-CD, whose structures are shown in Figure 1, were purchased from Aldrich.

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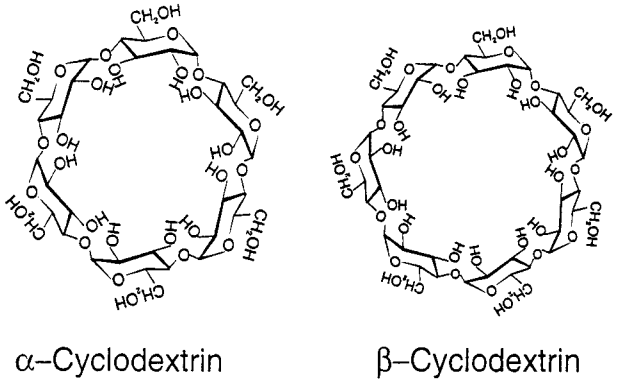

Figure 1. Structures of α-cyclodextrin and *β*-cyclodextrin.

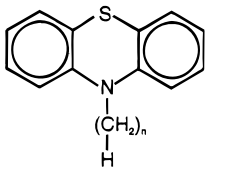

Figure 2. Structure of *N*-alkylphenothiazines (PC$_n$, $n = 3$, 9, 12, 16).

SDS was used after recrystallization from ethanol three times followed by washing with ethyl ether and drying at 50 °C under moderate vacuum. α- and *β*-CDs were used without further purification. The PC$_n$ ($n = 3$, 9, 12, 16) materials were synthesized as previously described,[8] and their structures are shown in Figure 2. D_2O was purchased from Aldrich and was deoxygenated by bubbling with nitrogen for at least 20 min before use.

Sample Preparations. Stock solutions of PC$_n$ were prepared in chloroform. The exact concentration was measured with optical absorption spectroscopy using a Perkin-Elmer 330 spectrophotometer ($\lambda_{max} = 312$ nm in chloroform, $\log \epsilon = 3.71$ M^{-1} cm^{-1}).[28] A stock micellar solution of 0.1 M SDS was prepared in deoxygenated deuterium oxide. Each micellar sample solution of PC$_n$ was prepared by transferring 70 μL of each PC$_n$ stock solution into a 16 mm o.d. × 125 mm long 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 thin film had formed, 1 mL of 0.1 M SDS micellar solution in D_2O was added to each 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 concentrations of PC$_n$ of the resulting micellar aqueous solutions were measured as 6.0×10^{-4} M with optical absorption spectroscopy. Each SDS micellar solution with 0, 5, 10, 15, and 20 mM cyclodextrins was prepared by dissolving equivalent amounts of α- and *β*-cyclodextrin into the micellar sample solutions. The solubilities of cyclodextrins in the SDS micellar solution exceeded the limits of α- and *β*-cyclodextrin in aqueous solution of 0.15 and 0.016 M, respectively.[21,22] This is verified by the resulting clear SDS solutions after solubilization of the cyclodextrins.

Photolysis. The samples for photolysis were prepared by taking 100 μL of each solution and transferring it into 2 mm i.d. × 3 mm o.d. Suprasil quartz tubes which were flame-sealed at one end. The tubes were shaken to equilibrate the solution, and then the samples were rapidly frozen by plunging into liquid nitrogen. All of the experiments were carried out at 77 K because ESEM requires solid-state systems.[19,20] Much previous work has shown that the micellar and vesicular structures are retained in rapidly frozen aqueous solutions.[19,29−34] Photoirradiation at 77 K was carried out with a 300 W xenon lamp (ILC-LX 300 UV). A 10 cm water filter and a Corning no. 7-54 filter (240 nm < λ < 410 nm) were placed in the light path to give 70% transmittance at 310 nm. The photoyield of the phenothiazine cation radical reached a plateau after 10 min of photolysis. ESR experiments were carried out following 10 min irradiation of the sample solutions, but ESEM experiments were carried out after 5 min irradiation because of secondary radical formation. The light intensity at the sample position was measured with a YSI-Kettering model 65 radiometer and was 1.1×10^{-3} W·m^{-2}. The Dewar holding the sample tube was rotated at 4 rpm during photolysis to ensure even irradiation of the samples.

Magnetic Resonance Experiments and Data Manipulations. ESR spectra were recorded at X-band using a Bruker ESP 300 spectrometer with 100 kHz field modulation. The irradiated sample 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 modulation field amplitude, 20 mT sweep width, seven scan accumulations, 56 s scan time constant, microwave frequency of 9.495 GHz, and 1.25×10^6 receiver gain. The photoinduced phenothiazine cation radical yield was determined by double integration of the ESR spectra using the ESP 1600 software. Each relative photoyield value is an average of the triple determinations and normalized by dividing by the photoyields from the sample of $PC_{16}/SDS/D_2O$ without cyclodextrin.

Two-pulse ESEM signals were recorded at 4.2 K with a home-built electron spin echo spectrometer operated at X-band using 40 and 80 ns excitation pulses.[4,19,20] 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 E501 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 microcomputer 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 baseline at the same interpulse time.[19,20,33] The simulations of the ESE signals were carried out with ESFT software with a constant isotropic coupling constant (A_{iso}) of 0.1 MHz, by optimizing the dipolar interaction distance (*R*) and the number (*N*) of interacting deuterium nuclei with the photoproduced phenothiazine cation radical. The more detailed theory and simulation procedures are described elsewhere.[20,29−33]

Results and Discussion

CDs have been used as chelating agents for several organic molecules via their macrocyclic cavities.[25,35−37] The tendency of CDs to house guest molecules results in two very important properties. One is their capability to protect, stabilize, or solubilize guest molecules; the other is their ability to selectively orient them. As CDs have no toxic effects, the first capability is of great value to the food, drug, and agricultural industries.[38−41] The second is the basis of their catalytic properties, which is of

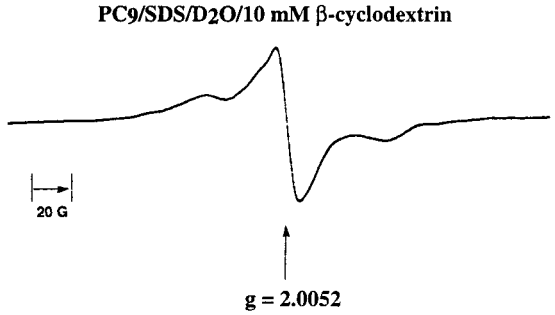

Figure 3. ESR spectrum at 77 K of a PC_6/SDS/D_2O/β-CD sample after 10 min photoirradiation at 77 K.

great interest for chemists who study enzyme mechanisms.[21] Due to its cavity size, β-CD and its derivatives are the most interesting CDs to form inclusion complexes with surfactant alkyl tails. In spite of their low solubilities in water (0.15 M for α-CD, 0.016 M for β-CD, and 0.18 M for γ-CD), the application of CDs has grown rapidly in the last decade by attaching hydrophilic functional groups to increase their solubility.[21,22] The association of CDs with surfactant alkyl chains has been intensively studied with conductometric, potentiometric, surface tensiometric, NMR, and fluorescence techniques.[23−27,42−48] The surfactant complexation with CDs changes critical micelle concentrations and micellar aggregation numbers.

In the present study photoinduced electron transfer from PC_n to interface water is studied by varying the pendant alkyl chain length of PC_n and the concentration of α- and β-CDs. The photoinduced electron transfer results in a phenothiazine cation within a SDS micelle and a solvated electron in the interface water. Further reaction of the solvated electron was already reported.[49] A representative ESR spectrum for PC_9/SDS/D_2O/10 mM β-CD is shown in Figure 3. The phenothiazine cation radical at 77 K is identified by a singlet with a **g** factor of 2.0052. The side multiplet lines were previously reported as due to surfactant alkyl chain radicals.[8−10,13] A pink color appears in the photoirradiated sample which is also characteristic of photoproduced phenothiazine cation radical. The color intensity reaches a maximum after about 10 min photoirradiation. The doubly integrated ESR signal intensity at $\mathbf{g} = 2.0052$ also reaches a plateau after 10 min photoirradiation.

Samples which do not include phenothiazine show no ESR signal. This indicates that the phenothiazine is the only photosensitive material absorbing in the 280 nm $< \lambda <$ 410 nm range as found before.[8−10]

The photoproduced phenothiazine cation radical quantities are defined as photoyields. The photoyields of PC_n in SDS/D_2O micelles versus the concentration of added α-CD are shown in Figure 4. The photoyields of PC_n versus the pendant alkyl chain length show a linear increase with increasing pendant alkyl chain length.

The decreasing photoyield trend versus concentration of α-CD suggests an increased electron transfer distance between the phenothiazine moiety and water at the micellar interface. This can be interpreted as due to intercalation of α-CD into the micellar interface to replace some water in the headgroup region. This interpretation is supported by the decrease in the normalized deuterium modulation depths versus the concentration of α-CD shown in Figure 5. The monotonic decrease of deuterium modulation depth with α-CD concentration indicates that the interaction of α-CD with surfactant molecules in SDS micelles does not critically affect the interface structure. Similar results were reported in studies of the addition of urea and its derivatives.[17,18]

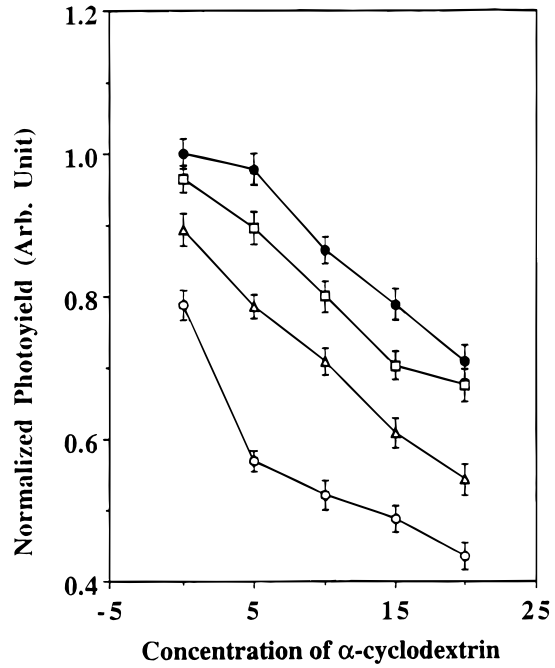

Figure 4. Normalized photoyields at 77 K of PC_3 (○), PC_9 (△), PC_{12} (□), and PC_{16} (●) in SDS/D_2O micelles versus the mM concentration of α-cyclodextrin after 10 min photoirradiation at 77 K.

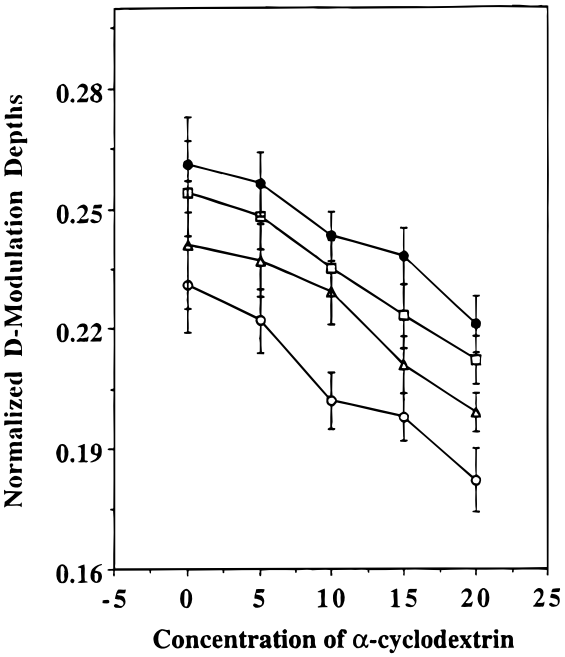

Figure 5. Normalized deuterium modulation depths at 77 K of PC_3 (○), PC_9 (△), PC_{12} (□), and PC_{16} (●) in SDS/D_2O micelles versus the mM concentration of α-cyclodextrin after 10 min photoirradiation at 77 K.

The results obtained from β-CD addition into SDS micelles are shown in Figures 6 and 7. The photoyields of PC_n in SDS/D_2O micelles versus the concentration of added β-CD are shown in Figure 6. The photoyield increases up to 10 mM β-CD and thereafter monotonically decreases until 20 mM β-CD. This contrasts with α-CD addition. The deuterium modulation depths of PC_n in SDS/D_2O micelles versus β-CD concentration are shown in Figure 7. The deuterium modulation depths increase to 10 mM β-CD, decrease to 15 mM, and then increase again to 20 mM. A comparative study on the interaction of SDS with α- and β-CDs indicates that β-CD has a greater association constant due to its greater cavity size and the hydrophobicity of its interior.[25] The interaction of CDs with SDS micelles

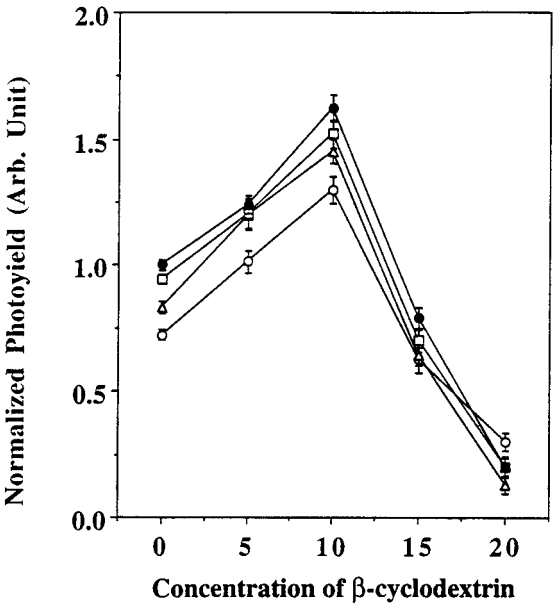

Figure 6. Normalized photoyields at 77 K of PC_3 (○), PC_9 (△), PC_{12} (□), and PC_{16} (●) in SDS/D_2O micelles versus the mM concentration of β-cyclodextrin after 10 min photoirradiation at 77 K.

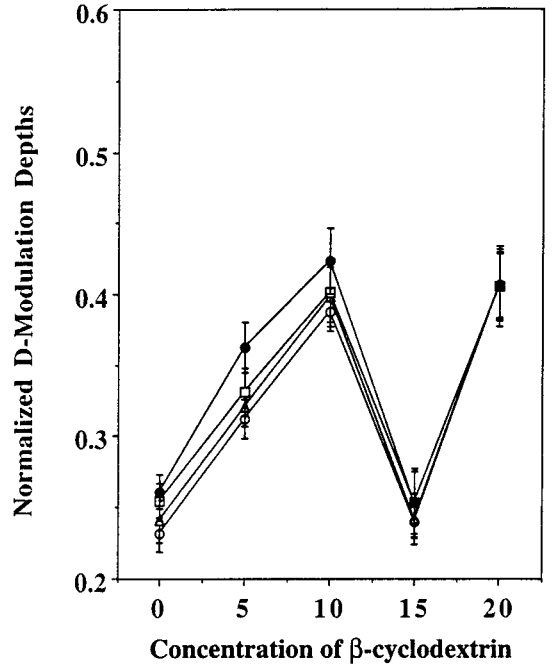

Figure 7. Normalized deuterium modulation depths at 77 K of PC_3 (○), PC_9 (△), PC_{12} (□), and PC_{16} (●) in SDS/D_2O micelles versus the mM concentration of β-cyclodextrin after 10 min photoirradiation at 77 K.

should be less than with SDS molecules because the bulkier micelle should constrain the interaction.

The increased photoyield of PC_n up to 10 mM β-CD is different from the decreased photoyield for α-CD. This is postulated as due to complexation of β-CD to SDS molecules in the headgroup region as shown in Figure 8. This allows some interface water to intercalate, which results in a shorter interaction distance between the phenothiazine moiety and micellar interface water. α-CD is too small to effectively complex an SDS molecule within a micelle. The decreased photoyield of PC_n with increasing α-CD concentration above 10 mM is interpreted as replacement of some interface water molecules to increase the electron transfer distance. The decreased photoyield from 10 to 15 mM β-CD can also be

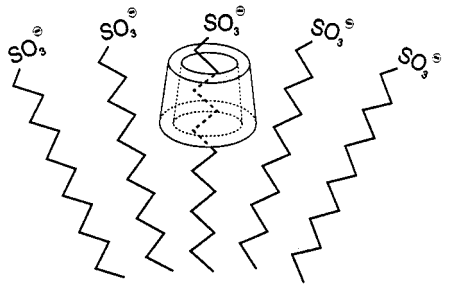

Figure 8. Schematic drawing of the complexed structure of β-cyclodextrin with SDS surfactant molecule.

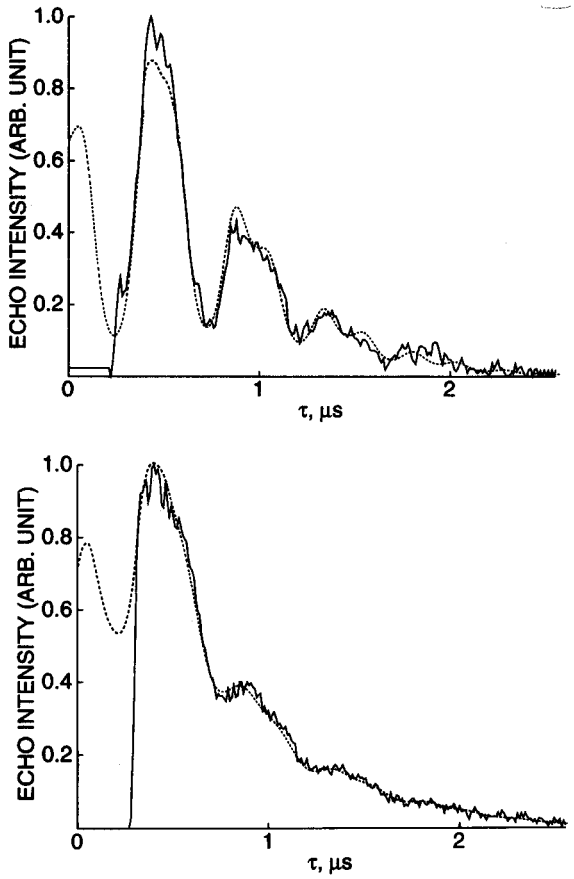

Figure 9. Two-pulse X-band ESE signals of PC_9 in SDS/D_2O micelles with (top) 20 mM and (bottom) 5 mM β-cyclodextrin. Experimental (—) and computer-simulated (···) signals are shown with fitting parameters of (top) $N = 6$ and $R = 3.0$ Å and (bottom) $N = 10$ and $R = 4.4$ Å.

interpreted as the effect of β-CD now replacing some interface water molecules. This interpretation is supported by the decreased deuterium modulation depths above 15 mM β-CD.

Addition of 20 mM β-CD results in significantly decreased photoyields. This is tentatively interpreted as due to partial dissociation of the SDS micelles by the high concentration of β-CD. This is supported by the unexpectedly large deuterium modulation depths at 20 mM indicating a short dipolar interaction distance ($R = 3.0$ Å) between the photoproduced phenothiazine cation radical and deuterium nuclei in the D_2O solvent. This is shown by the simulation of the ESEM spectra in Figure 9. The aggregated and partially dissociated micellar structures show deuterium interaction distances of 4.4 and 3.0 Å, respectively.

Conclusions

The photoinduced charge separation efficiency of PC_n in SDS/D_2O micelles by electron transfer from the phenothiazine moiety

to interface water through the micellar interface was modified by the addition of α- and β-CDs. The photoyields versus the α-CD concentration show a monotonic decrease. This is interpreted as an increased electron transfer distance from the phenothiazine moiety to interface water by replacement of some of the water molecules at the interface by α-CD. This is confirmed by a decreased deuterium modulation depth from D_2O. The photoyields of PC_n versus the β-CD concentration increase to 10 mM and thereafter decrease to 20 mM. The increased photoyields up to 10 mM are interpreted as due to a decreased interaction distance from the phenothiazine moiety to interface water by intercalation of β-CD between the headgroups of SDS surfactant molecules in the micelle. The decreased photoyield between 10 and 15 mM β-CD is assigned to an increased interaction distance for electron transfer which is confirmed by a decreased deuterium modulation depth from D_2O in this concentration range. A decreased photoyield above 15 mM β-CD is observed and correlates with an increased deuterium modulation depth from D_2O. This is interpreted as partial dissociation of the micellar structure above 15 mM β-CD which is confirmed by the increased deuterium modulation depths above 15 mM β-CD. The distinct differences in photoyields and deuterium modulation depth trends between α- and β-CDs are due to their different cavity sizes and hydrophobicities.

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