Alkyl Chain Length Effects on the Photoionization of N-Alkylphenothiazines and Sulfonated Alkylphenothiazines in Anionic Alkyl Sulfate and Cationic Alkyltrimethylammonium Bromide Micelles

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The photoionization yields of *N*-alkylphenothiazines solubilized in either cationic or anionic micelles at 77 K were studied as a function of both alkyl and surfactant chain length. The results are compared to similar work on sulfonated *N*-alkylphenothiazines. The location of the phenothiazine moiety with respect to the micelle–water interface together with cation–water interactions is a major factor controlling the photoionization efficiency. The position of the *N*-alkylphenothiazine chromophore within a micelle can be altered by changing the alkyl chain length. The photoefficiency is also affected by the surface charge of the micelle.

Introduction

Photoionization of chromophores in organized molecular assemblies, such as micelles or vesicles, is commonly used as a model system for artificial photosynthesis.[1-4] Such surfactant systems compartmentalize the electron-transfer processes and permit control of net charge separation across an interface.

Photoionization and charge separation processes in these molecular assemblies are significantly affected by several structural factors. It has been shown that the monophotonic photoionization yield of *N,N,N',N'*-tetramethylbenzidine (TMB) in a frozen aqueous micellar solution is dependent on the micellar counterions, the size and shape of the micelle, the micellar charge, the presence of alcohols or crown ethers that affect the micellar surface charge density, and the structure of the micellar interface.[5-14]

Recent kinetic studies based on the oxidative quenching of excited triplets of the [5,10,15,20-tetrakis(4-sulfonatophenyl)-porphinato]zinc(II) ion by alkylmethyl viologen derivatives solubilized in dihexadecyl phosphate vesicles suggest that the electron-accepting rate is dependent on the alkyl viologen chain length. This observation was confirmed by electron spin–echo modulation studies of photoreduced alkylmethyl viologen cation radicals in frozen vesicle solutions.[15,16] The length of the alkyl chain governs the solubility of the molecule in the vesicle. An optimal photoionization yield has been found for alkylruthenium complexes with hexamethyl and octylmethyl viologen as electron acceptors when compared to shorter or longer alkyl chain analogues solubilized in sodium dodecyl sulfate micellar solutions.[17] The photoionization efficiency of *N*-alkylphenothiazinesulfonates in both sodium alkyl sulfate and alkyltrimethylammonium bromide frozen micellar solutions is also dependent on the alkyl chain length of both the photoacceptor and the micelle surfactant.[18] Since the location of the chromophore with respect to the micelle interface is one of the important factors that determines the net charge separation efficiency, it is important to try and optimize this variable.

When the phenothiazine ring system is sulfonated, the negative sulfonate group anchors the phenothiazine moiety near the micellar interface. In this study, unsubstituted *N*-alkylphenothiazines were used to penetrate more deeply into a micelle. The photoionization efficiency was determined by electron spin resonance, ESR, and the penetration into the micellar core was measured by electron spin–echo modulation, ESEM, spectroscopy.

Experimental Section

Materials. Five *N*-alkylphenothiazines (PC_n, see Figure 1) were synthesized by using a modified literature procedure.[19]

Ethylphenothiazine and Propylphenothiazine. A solution of 0.996 g (5 mmol) of phenothiazine (Aldrich, 98+%, used without further purification), 1.405 g of ethyl bromide or 1.559 g of propyl bromide (13 mmol, Aldrich, 97%, used without further purification), 0.169 g (0.5 mmol) of *n*-tetrabutylammonium hydrogen sulfate (Aldrich, 98%, used without further purification), and 20 mL of methyl isobutyl ketone (MIK), which was purified before use, was stirred vigorously with 20 mL of 50% aqueous sodium hydroxide solution for 24 h at room temperature. This step was followed by refluxing the solution for 24 h. The progress of the reaction was monitored with thin-layer chromatography (TLC, Aldrich silica gel, *n*-hexane:petroleum ether = 15:1, v:v). When all of the phenothiazine was consumed, the reaction was quenched by pouring the solution into a separatory funnel, followed by the addition of 50 mL of deionized water and 20 mL of MIK. The organic layer was separated, and the aqueous layer was washed with MIK. The combined organic extracts were washed with water, and the wet organic solution was dried over anhydrous magnesium sulfate for 7 h. The remaining solvent was evaporated under reduced pressure. The resulting crude solid products were dissolved in 0.5 mL of petroleum ether and separated by flash column chromatography (Aldrich silica gel, 230–400 mesh, 60 Å, *n*-hexane:petroleum ether = 15:1, v:v). The yields of ethylphenothiazine and propylphenothiazine were 1.044 g (92%) and 1.073 g (89%), respectively. The compounds were identified with UV/visible spectroscopy on a Varian Techtron 635 spectrophotometer, by NMR spectroscopy on a General Electric QE-300,

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(1) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.
(2) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7.
(3) Hurly, J. K.; Tollin, G. *Sol. Energy* **1982**, *28*, 187.
(4) Kevan, L. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part B, pp 329–384.
(5) Narayana, P. A.; Li, A. S.; Kevan, L. *J. Am. Chem. Soc.* **1982**, *104*, 6502.
(6) Arce, R.; Kevan, L. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1025.
(7) Szajdzinska-Pietek, E.; Maldonado, D.; Kevan, L.; Jones, R. R. M. *J. Am. Chem. Soc.* **1984**, *106*, 4675.
(8) Maldonado, R.; Kevan, L.; Szajdzinska-Pietek, E.; Jones, R. R. M. *J. Chem. Phys.* **1984**, *81*, 3985.
(9) Baglioni, P.; Kevan, L. *J. Phys. Chem.* **1987**, *91*, 2101.
(10) Baglioni, P.; Kevan, L. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 467.
(11) Baglioni, P.; Kevan, L. *Prog. Colloid Polym. Sci.* **1988**, *76*, 183.
(12) Rivara-Minten, E.; Baglioni, P.; Kevan, L. *J. Phys. Chem.* **1988**, *92*, 2613.
(13) Baglioni, P.; Rivara-Minten, E.; Kevan, L. *J. Phys. Chem.* **1988**, *92*, 4726.
(14) Baglioni, P.; Rivara-Minten, E.; Kevan, L. *J. Phys. Chem.* **1989**, *93*, 1570.
(15) Thompson, D. H. P.; Barrette, W. C., Jr.; Hurst, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2003.
(16) Hurst, J. K.; Thompson, D. H. P.; Connolly, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 507.
(17) Baglioni, P.; Hu, Ming; Kevan, L. *J. Phys. Chem.* **1990**, *94*, 2586.
(18) Hu, M.; Kevan, L. *J. Phys. Chem.* **1990**, *94*, 5348.
(19) Gozlan, I.; Ladkani, D.; Halpern, M.; Rabinovitz, M.; Anoir, D. *J. Heterocyclic Chem.* **1984**, *21*, 613.

0022-3654/91/2095-7944$02.50/0

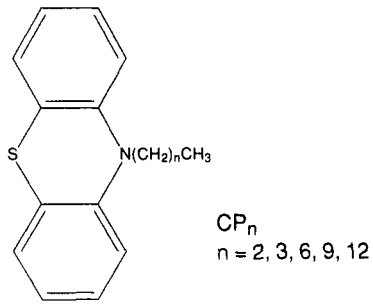

Figure 1. Structure of *N*-alkylphenothiazine.

and with mass spectrometry on a VG-70-SEQ-300 mass spectrometer.

Hexylphenothiazine. A solution of 0.996 g (5 mmol) of phenothiazine, 2.146 g (13 mmol) of hexyl bromide, 0.169 g (0.5 mmol) of *n*-tetrabutylammonium hydrogen sulfate, and 20 mL of MIK was stirred vigorously with 20 mL of 50% aqueous sodium hydroxide solution for 32 h at room temperature and then refluxed for 2 days. The progress of the reaction was monitored by TLC (Aldrich silica gel, *n*-hexane:petroleum ether = 15:1, v:v). When all of the phenothiazine was consumed, the reaction was quenched by pouring the solution into a separatory funnel, followed by the addition of 50 mL of deionized water and 20 mL of MIK. The organic layer was separated, and the aqueous layer was washed with MIK. The combined organic extracts were washed with water, and the wet organic solution was dried over anhydrous magnesium sulfate for 7 h. The remaining solvent was removed by evaporation under reduced pressure. The resulting crude oily product was separated by flash column chromatography (Aldrich silica gel, 230–400 mesh, 60 Å, *n*-hexane:petroleum ether = 15:1, v:v). The yield of *N*-hexylphenothiazine was 1.079 g (76%). The compound was identified with UV/visible spectroscopy, NMR spectroscopy, and mass spectrometry.

Nonylphenothiazine and Dodecylphenothiazine. A solution of 0.996 g (5 mmol) of phenothiazine, 2.693 g (13 mmol) of nonyl bromide or 3.240 g of dodecyl bromide, 0.169 g (0.5 mmol) of *n*-tetrabutylammonium hydrogen sulfate, 0.132 g (0.5 mmol) of 18-crown-6 ether (Aldrich, 99.5%, Gold label), and 20 mL of MIK was stirred vigorously with 20 mL of 50% aqueous sodium hydroxide solution for 2 days at room temperature. This step was followed by refluxing the mixture for 4 days. The progress of the reaction was monitored by TLC (Aldrich silica gel, *n*-hexane: petroleum ether = 15:1, v:v). When all of the phenothiazine was consumed, the reaction was quenched by pouring the solution into a separatory funnel, followed by the addition of 50 mL of deionized water and 20 mL of MIK. The organic layer was separated, and the aqueous layer was washed with MIK. The combined extracts were washed with water, and then the wet organic solution was dried over anhydrous magnesium sulfate for 7 h. The remaining solvent was evaporated at reduced pressure. The resulting crude oily products were separated by flash column chromatography (Aldrich silica gel, 230–400 mesh, 60 Å, *n*-hexane:petroleum ether = 15:1, v:v). The yields of nonylphenothiazine and dodecylphenothiazine were 1.222 g (75%) and 1.323 g (72%), respectively. Each of the products was identified with UV/visible spectroscopy, NMR spectroscopy, and mass spectrometry.

Stock Micellar Solutions. Sodium decyl sulfate ($NaC_{10}SO_4$) was obtained from Eastman Kodak; sodium dodecyl sulfate and sodium tetradecyl sulfate ($NaC_{12}SO_4$ and $NaC_{14}SO_4$) were obtained from Aldrich. These compounds were recrystallized three times from ethanol, washed with ethyl ether, and dried at 50 °C under a moderate vacuum. 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.

Preparation of the Samples. For each alkylphenothiazine, 2.5 × 10^{-4} mol were added to 25 mL of chloroform. The concentration of each of the solutions was checked by using UV/visible spectroscopy (λ_{max} = 320 nm; log ϵ = 3.71 M^{-1} cm^{-1})[20] 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 blowing nitrogen gas onto the surface of the solution, which resulted in the formation of a thin film of *N*-alkylphenothiazine on the walls of the sample vial. One milliliter of the 0.1 M micellar stock solution was then added to the sample vial. Argon gas was blown onto the surface of the mixture for 5 min. The samples were then sonicated with a Fisher Model 300 sonic dismembrator operated at 35% relative output with a 4-mm-o.d. microtip under nitrogen gas flow at 58 ± 3 °C for 5 min. After sonication, the concentration of phenothiazine was again checked by UV/visible spectroscopy; the concentration was found to be 4 × 10^{-4} M. The samples were then thermostated at 50 ± 3 °C for 3 h (i.e., above the surfactant Kraft point). Clear solutions were obtained, which indicated complete solubilization of the *N*-alkylphenothiazines. The samples were then placed in 2-mm-i.d. × 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.

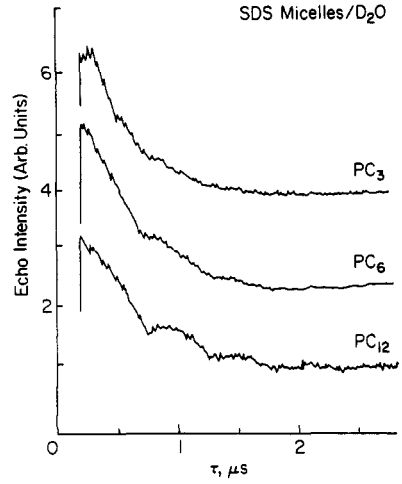

Figure 2. Two-pulse ESE signals at 4.2 K of photoionized PC_3, PC_6, and PC_{12}, solubilized in sodium dodecyl sulfate micelles. The signals are offset vertically.

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 photoyield was normalized to the yield for *N*-dodecylphenothiazine solubilized in the decyltrimethylammonium bromide micellar system.

Two-pulse electron spin–echo deuterium modulation signals were recorded at 4.2 K on a home-built spectrometer using 40-ns excitation pulses.[21] 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.[8]

Results

Two-pulse ESE decay signals at 4.2 K for three *N*-alkylphenothiazine radical cations solubilized in sodium decyl sulfate micelles are shown in Figure 2. The signals show a modulation with a 460-ns period, characteristic of the deuterium Larmor precession in a 3.3-kG magnetic field. The photoyield data at

(20) Hanson, P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, *3*, 264.
(21) Ichikawa, T.; Kevan, L.; Narayana, P. A. *J. Phys. Chem.* **1979**, *83*, 3378. Narayana, P. A.; Kevan, L. *Magn. Reson. Rev.* **1983**, *87*, 239.

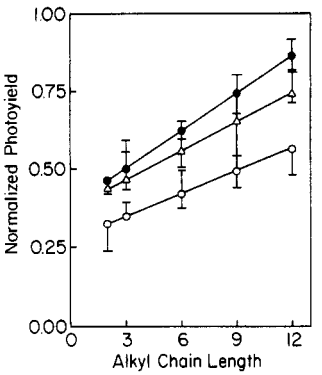

Figure 3. Normalized PC_n photocation yield, measured by ESR at 77 K, as a function of PC_n alkyl chain length for sodium alkyl sulfate micelles. Error bars indicate the standard deviation (× = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates).

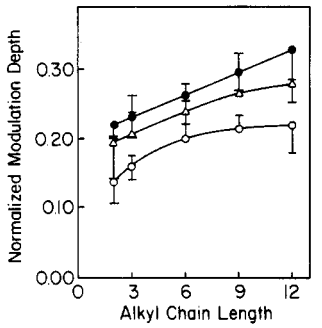

Figure 4. Normalized deuterium modulation depth at 4.2 K as a function of PC_n alkyl chain length in micellar solutions of sodium alkyl sulfates (× = C_{10}, △ = C_{12}, ○ = C_{14} alkyl sulfates).

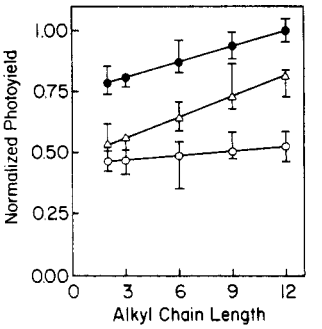

Figure 5. Normalized PC_n photoyield, measured by ESR at 77 K, as a function of PC_n alkyl chain length in micellar solutions of alkyltrimethylammonium bromides (× = C_{10}, △ = C_{12}, ○ = C_{14} alkyltrimethylammonium bromides).

77 K for the PC_n^+ cations in sodium alkyl sulfate micellar solutions versus PC_n alkyl chain length are given in Figure 3. Figure 4 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. Figure 5 shows the photoyield at 77 K of PC_n^+ versus alkyl chain length for three alkyltrimethylammonium bromide micellar systems. The normalized deuterium modulation depths for these systems are plotted in Figure 6.

Discussion

The photolysis yield of *N*-alkylphenothiazine solubilized within a micelle is affected by the location of the molecule 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^+).[22] The *g* factor of the ESR

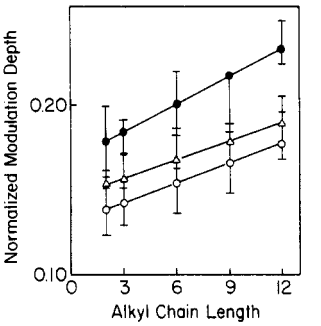

Figure 6. Normalized deuterium modulation depth at 4.2 K as a function of PC_n alkyl chain length in micellar solutions of alkyltrimethylammonium bromides (× = C_{10}, △ = C_{12}, ○ = C_{14} alkyltrimethylammonium bromides).

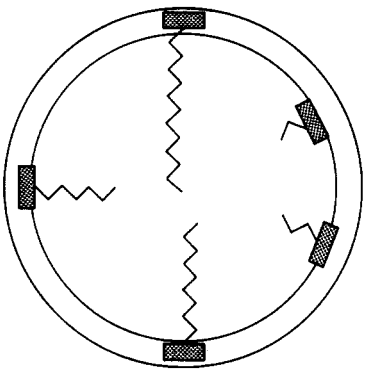

Figure 7. Schematic representation of the locations of PC_n within a micelle; the rectangle represents the phenothiazine moiety; the outer large circle represents the surface of the micelle; the inner circle represents a distance of 0.6 nm from the micelle surface.

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,[23] $g = 2.0053$ for phenothiazine,[24] and $g = 2.0059$ for propylphenothiazinesulfonate.[25]

The photoyield data of these *N*-alkylphenothiazine derivative cations display several trends in Figures 3 and 5. 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.[4] 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 cation 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 Figures 4 and 6. The normalized deuterium modulation depths increase with increasing alkyl chain length of the cation. Also the normalized modulation 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 Figures 4 and 6 of increasing modulation depth with increasing alkyl chain length on the alkylphenothiazines can be explained by movement of the phenothiazine moiety from the

(22) Alkaitis, S. A.; Beck, G.; Gratzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723.
(23) Clark, D.; Gilbert, B. C.; Hanson, P.; Kirk, C. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, *10*, 1103.
(24) Galasso, V. *Gazz. Chim. Ital.* **1976**, *106*, 457.
(25) Sakaguchi, M.; Hu, M.; Kevan, L. *J. Phys. Chem.* **1990**, *94*, 870.

micelle interior toward the interface region where it interacts 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 $C_{10} > C_{12} > C_{14}$. Previous work has shown that the polarity of the interface of sodium alkyl sulfate micelles decreases as the surfactant chain length increases.[25-27] Furthermore, a departure from the standard model of a micelle (oillike core surrounded by a charged bilayer surface) occurs if the surfactant chain length is shorter than about 10 carbons.[28,29] 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 ($N_0 = 50$) than either dodecyl ($N_0 = 62$) or tetradecyl ($N_0 = 118$) sulfate.[30,31] A more open interface results in greater water penetration into the micellar interface. These points explain why the deuterium modulation depth observed for the sodium decyl sulfate is consistently greater than that for either the dodecyl 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;[4,32] 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 interactions between the water and the photoproduced cation.

The results obtained on the N-alkylphenothiazines differ from those for alkylphenothiazinesulfonates or phenothiazinylalkanesulfonates in anionic micelles.[17] For the alkylphenothiazinesulfonates (C_nPSO_3), the normalized modulation depth decreased slightly while the radical yield increased with the alkyl chain length was increased from 1 to 12 carbons. These ESE results were explained in terms of an increased alkyl chain on the phenothiazine changing the hydrophilic/lipophilic balance, allowing the phenothiazine moiety to be solubilized deeper into the micelle and further away from the interface region than a more polar derivative. Furthermore, as the alkyl chain on the phenothiazine is increased and the molecule is pulled toward the micellar core, back electron transfer is inhibited. This results in an increase in the net photoyield of the radical. ESEM showed that methylphenothiazinesulfonate was located on or near the surface of the micelle from the magnitude of the normalized modulation depth for the alkylphenothiazinesulfonates.

For the phenothiazinylalkanesulfonates, PC_nSO_3, PC_6S showed a maximum photoyield and deuterium modulation depth in sodium decyl and dodecyl sulfate micellar solutions while a monotonic trend occurs for PC_nSO_3 in sodium tetradecyl sulfate. This is explained by bending of the alkyl chains. A bent C_6 chain allows the phenothiazine moiety to better probe the micellar interface. A bent C_{12} chain does likewise but also introduces more flexibility so that the phenothiazine moiety is slightly better solubilized by the surfactant alkyl chains.

The different results for the N-alkylphenothiazines compared to the sulfonated alkylphenothiazines can be explained as follows. The smaller modulation depth compared with both of the sulfonated alkylphenothiazines indicates a longer mean distance of the cation radicals from the deuterium nuclei in the water phase. Thus, the phenothiazine moiety of N-alkylphenothiazine is buried deeper into an anionic micelle due to higher lipophilicity compared to their sulfonated analogues. The different trends of radical yield and modulation depth with the alkyl chain length in C_nP compared with C_nPSO_3 is related to the polar sulfonate group on the phenothiazine ring. The trend of radical yields in PC_n is consistent with that of C_nPSO_3 due to back electron transfer for the latter. With phenothiazinylalkanesulfonates, the different relative sequences of the photoyield and deuterium modulation depth are associated with the bending of the alkyl chain and the polar headgroup on the end of the alkyl chain of PC_nSO_3.

A similar trend is observed in the alkyltrimethylammonium bromide cationic systems. As the alkyl chain on the phenothiazine is increased, the normalized modulation depth also increases; however, this increase is not as pronounced as in an anionic micellar system. This result is consistent with other comparative studies on anionic and cationic micelles and shows not only that the photoyield in cationic micelles depends on the degree of water penetration and location of the chromophore with respect to the interface but that other positional factors are involved.

Figure 7 is an illustration of possible locations of N-alkylphenothiazines within micelles. The outer circle represents the exterior of the interface region. A concentric circle, 0.6 nm from the interface region, is also shown. Since 0.6 nm is the approximate limiting interaction distance for electron–nuclear modulation of an ESE decay pattern, any paramagnetic species located further than 0.6 nm from the interface will show little or no deuterium modulation. Since both ethyl- and propylphenothiazine give extremely weak deuterium modulation (see Figure 2), these molecules are located furthest from the interface. Dodecylphenothiazine, which has the strongest deuterium modulation, is located nearest to the interface.

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 tetradecyl sulfate and in decyl-, dodecyl-, and 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 that 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 versus anionic micelles. This increase is attributed to a lower energy barrier for a photoejected electron to traverse a cationic micelle interface. A comparison of the deuterium modulation depths with those from a phenothiazine radical sulfonated on the ring shows that the unsubstituted N-alkylphenothiazine is solubilized in a less polar environment, further from the micellar 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.

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(26) Ottavani, M. F.; Baglioni, P.; Martini, G. *J. Phys. Chem.* **1983**, *87*, 3146.
(27) Baglioni, P.; Ottaviani, M. F.; Martini, G.; Ferroni, E. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984; Vol. 1, pp 541–557.
(28) Baglioni, P.; Ferroni, E.; Martini, G.; Ottaviani, M. F. *J. Phys. Chem.* **1984**, *88*, 5107.
(29) Evans, D. F.; Ninham, B. W. *J. Phys. Chem.* **1983**, *87*, 5025.
(30) Baglioni, P.; Ottaviani, M. F.; Martini, G. *J. Phys. Chem.* **1986**, *90*, 5878.
(31) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.
(32) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.